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THE DEVELOPMENT OF A HIGH TEMPERATURE pH ELECTRODE FOR GEOTHERMAL FLUIDS

FINAL REPORT - TASK III AND YEAR END SUMMARY

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DEVELOPMENT OF A HIGH TEMPERATURE pH ELECTRODE FOR GEOTHERMAL FLUIDS

I. SUMMARY

This report summarizes work done to demonstrate the applicability of a stabilized zirconia pH sensor to high temperature measurements on brines containing as much as 20 weight percent NaCl and 100 ppm hydrogen sulfide. Throughout the program stable operation was achieved, and measured pH values were in good agreement with calculated values. Differences were generally less than 0.5 pH unit at 285°C, and it is not yet certain whether the discrepancies are associated with the measured or calculated values of the pH.

While some sensors failed through cracking or because of unperfected seals, no signs of chemical degradation of the ceramic were detected during tests at 285°C covering a range of pH between 3 and 9. Two sensors were operated at 285°C for periods of 11 days, and one was employed in successive tests for a total of 37 days. At the end of this period the sensor was still satisfactory, and it was forwarded to the sponsoring laboratory, PNL, for further tests.

Although most of the work was performed at 285°C a limited amount of testing was done at lower temperatures: 95, 150, and 225°C. Sensors prepared from in-house tubes and from tubes obtained from a new supplier performed well at 95°C for extended periods, in spite of earlier difficulties with the standard ceramic at this temperature. There is still, however, some uncertainty concerning the adequacy of our seals particularly in cycling between 285°C and lower temperatures.

In a brief experiment one sensor was operated satisfactorily at 285°C and 5000 psi pressure. (Normal operation was at 1200 psi.) A concept for a simple calibration system was also demonstrated.

It is concluded from this work that the present sensors should perform well in geothermal brines over a range of temperature if given sufficient attention to calibration and seal maintenance. Clearly, however, care must be exercised to obtain high quality ceramics, particularly with regard to surface integrity and freedom from surface pores. Improved seals between the ceramic tubes and the metal fittings are also required for long-term, routine use in the field.

II. INTRODUCTION

The Department of Energy (DOE) through PNL desires to develop electrical and electrochemical probes that can measure various environmental characteristics of fluids under high temperature-high pressure conditions in geothermal wells and associated piping. An important probe of this type is one that measures pH.

The General Electric Company has developed a new approach to such pH measurements in which an oxygen ion conducting ceramic membrane (e.g., stabilized zirconia) is employed in a sensor somewhat analogous to the glass electrode.(1) The new sensor retains the specificity of the glass electrode, is equally insensitive to interference from redox active species, and possesses markedly superior resistance to attack by aqueous media at high temperatures.

Although earlier work has established the feasibility of the concept, the performance of the new sensor has not been demonstrated under a wide variety of conditions. Work is therefore required to demonstrate its capability under specific conditions of practical interest; e.g., its applicability to measurements on geothermal brines which has been the focus of the present program.

Background on the state-of-the-art of the new sensor as well as details of the present program, as originally planned were thoroughly addressed in a design report submitted to PNL.(2) A major aim of the laboratory tests has been to demonstrate that the performance of the sensor does not suffer in the presence of hydrogen sulfide and high concentrations of saline. The test system, protocols and experimental results with simulated brines are discussed in the present report.

III. EXPERIMENTAL

A. Sensor Design

Figure 1 shows the structural details of the sensor used in most of the work. The ceramic was a 1/4 inch o.d. tube of yttria (8.0 wt. percent) stabilized zirconia. It was retained in a Conax Type EG-125 Gland with a seal consisting of Teflon, Vespel, silver and alumina elements as shown. On the basis of previous work we selected the dry copper/cuprous oxide mixture as our preferred internal junction over the previously employed aqueous internal junctions. This was done for several reasons: 1) we had found it to be readily prepared by simple mixing of the powders and packing into the tube; 2) when prepared in this fashion it had been found to be extremely stable and reproducible; 3) in contrast to aqueous internals it permits ready designation of the active region of the sensor because it does not wet the wall with a conducting film; and 4) in the absence of an internal aqueous phase, seal fabrication is simplified.

For the junction we employed a 1:1 (by weight) mixture of finely divided copper and cuprous oxide (Fisher Copper Metal-Electrolytic Dust, purified; Baker Cuprous Oxide Powder, Analyzed Reagent) to a depth of two inches. A 30 mil copper wire served as the contact and lead from the sensor.

B. Test Equipment

A diagram of the test system is shown in Figure 2. Fabricated of Titanium and glass it paralleled a stainless steel system used in Reference 1. Provision was made for pumping water, acid, base and simulated brines containing carbonate buffers and sulfides into the heated and pressurized titanium auto-

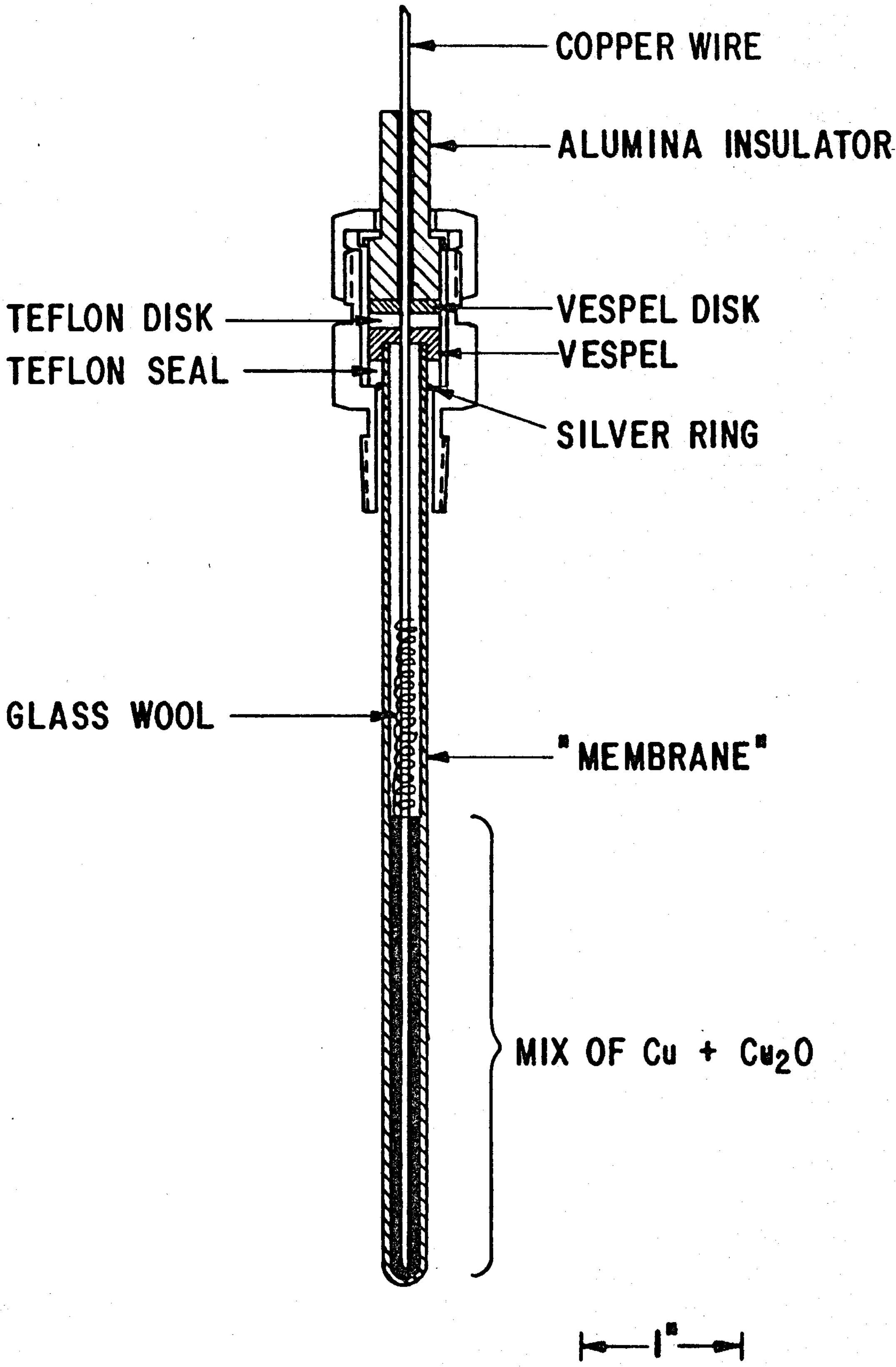

Figure 1. Schematic diagram of preferred sensor for use with geothermal brines.

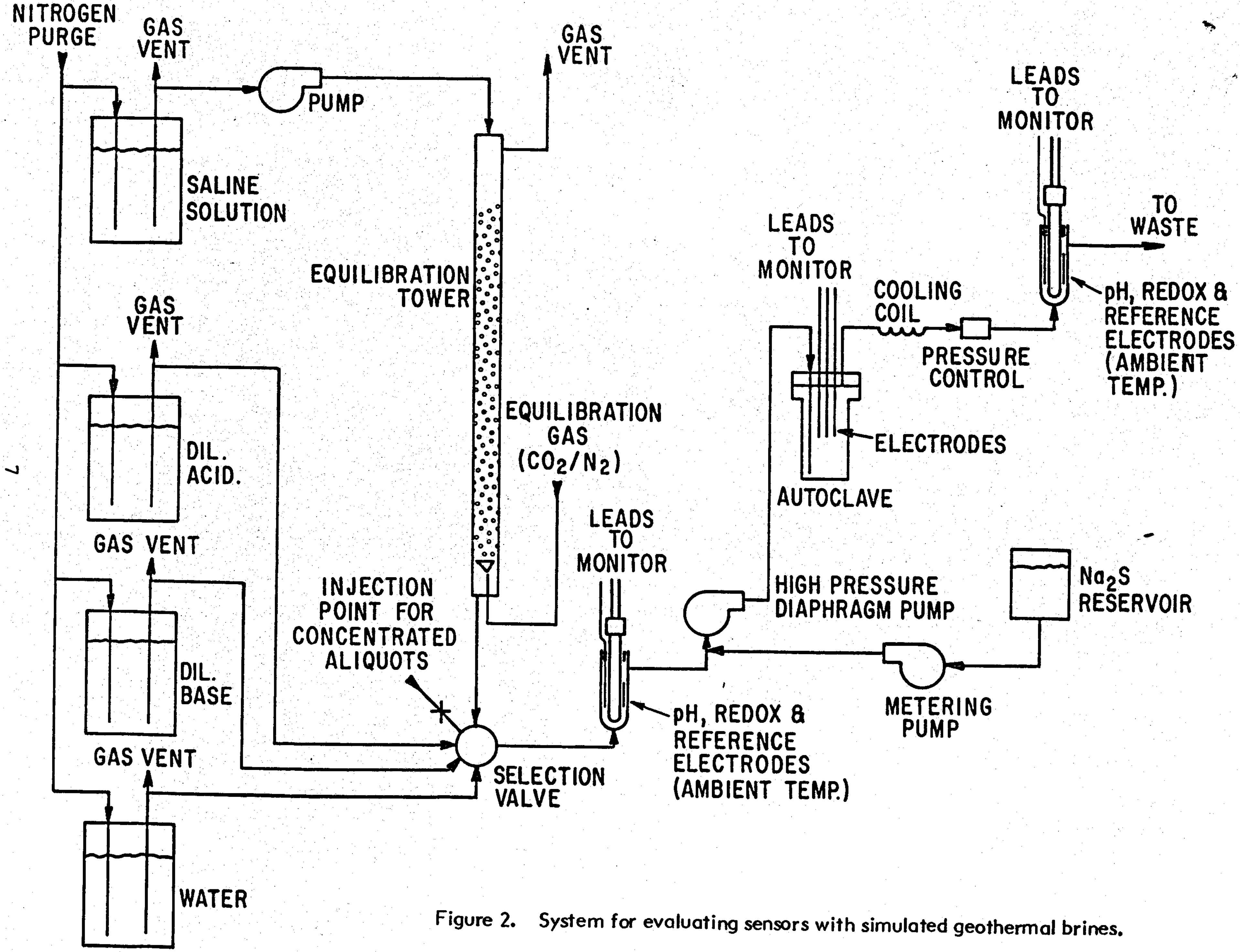

Figure 2. System for evaluating sensors with simulated geothermal brines.

clave which had a capacity of 1 liter. It was also possible to introduce aliquots of more concentrated acid or base to bring about more rapid changes in pH. The main pump was a Pulsfeeder Model LS-20 with a titanium head manufactured by the Interpace Corporation, Rochester, N.Y. All fittings and other parts of the pressurized section were also made of titanium.

Inserted into the head of the autoclave were the sensor, a platinized platinum electrode (for monitoring the redox potential of the solution) and two reference electrodes. The latter were essentially like those described by Danielson,(3) but we eliminated his zirconia thread. As a result bubbles that formed upon depressurization of the system during cooling resulted in open circuits.

All streams that entered the autoclave were purged with nitrogen to reduce the oxygen concentration to low levels. To control the pH of the brine solutions before they entered the autoclave they were contacted with carbon dioxide-nitrogen mixtures in a packed column following a procedure described by Syrett, et al.(4) The pH and redox potential of the solutions entering the autoclave were monitored at ambient conditions with a commercial glass electrode (Ingold) and a platinum flag, respectively, both referred to a common reference electrode. Similar measurements were made at ambient conditions on the stream emerging from the autoclave. In this way irreversible chemical changes occurring during passage through the autoclave could be detected. Provision was also made for sampling the streams and for checking the flow rate.

Rather than incorporate low concentrations of sulfide in the master feed solutions from which it might be lost through volatilization or oxidation, we elected to inject a more concentrated solution of sodium sulfide into the brine stream just before it entered the high pressure diaphragm pump. The injection point is indicated in Figure 2. A Harvard Syringe Pump Model 1100 with a 20 ml syringe was used for the injection.

Temperature of the autoclave was controlled with a Leeds and Northrup Electromax III proportional controller. High temperature pH and potential measurements were made with a Keithley Type 616 electrometer multiplexed with an Orion 855 Electronic Switch. The potentials of the pH sensor, the platinized platinum redox probe, the autoclave and the second reference electrode were all measured against the same primary reference electrode. The lower temperature measurements, pH and redox potential of the inlet and outlet streams to the autoclave, were made with an Orion Model 801 Digital pH meter, again multiplexed with an Orion Model 855 Electronic Switch. All potentials and the temperature were recorded on a Linear Instruments Corp. three channel recorder.

C. Test Protocols

The initial series of tests were designed to determine the stability of the sensors under a variety of conditions. It was planned that each test would extend over a period of several days and would involve the steps indicated in Table I. A key element is the exposure for several days to simulated brines covering a range of pH values.

In each case a calibration curve was obtained during the first two days by determining the response to a change from 1 millimolal HCl to 1 millimolal NaOH. Then the sensor was aged for about a week in a selected saline solution covering the range of conditions indicated in Table II. During this period

Table I

A TYPICAL TEST

Day 1	Start up on water
2	Water → 0.001 $\underline{m}$ HCl → 0.001 $\underline{m}$ NaOH → carbonate/saline/(H_2S)
3	Carbonate/saline/(H_2S)
4	Carbonate/saline/(H_2S)
5	Carbonate/saline/(H_2S)
6	Carbonate/saline/(H_2S)
7	Carbonate/saline/(H_2S)
8	Carbonate/saline/(H_2S)
9	Carbonate/saline/(H_2S) → change CO_2 level → water
10	Water → 0.001 $\underline{m}$ HCl → 0.001 $\underline{m}$ NaOH; off

Table II

RANGE OF CONDITIONS USED IN AGING TESTS AT 285°C*

Hi Saline (20% NaCl)				Lo Saline (0.2% NaCl)	
No H_2S		With H_2S		With H_2S	
Hi pH(a)	Lo pH(b)	Hi pH(c)	Lo pH(d)	Hi pH(e)	Lo pH(f)
1	2	3	4	5	6

a) 0.11m equivalent base/low CO_2
b) 0.034m equivalent base/high CO_2
c) 0.11m equivalent base/low CO_2
d) 0.034m equivalent base/high CO_2
e) 0.11m equivalent base/low CO_2
f) 0.034m equivalent base/high CO_2

---

*More detailed information concerning compositions will be found in Table VI and in Appendix B.

potentials were monitored to check for drift or degradation. The carbon dioxide level of the brine solution was then changed to induce a pH change and the response of the sensor was monitored and compared with the best estimate that could be made theoretically for the high ionic strength solutions involved. Finally, after an overnight flush of the system with water, the calibration curve was rechecked by determining the response of the sensor to a transition from one millimolal acid to one millimolal base. In a few runs additional steps were introduced into the test protocols. These will be discussed as they arise.

D. Sulfide Analysis

In order to control the sulfide concentration in the entering solution and to ascertain that it was maintained during passage through the autoclave, sulfide analyses are required on an occasional basis. For this purpose a colorimetric method involving the reduction of methylene blue was found satisfactory. The procedure is provided in the ''Methods Manual''(5) for a Hach Direct Reading Engineer's Laboratory, Model DR-EL/4, which was used for the analyses. With proper care to protect samples, reagents and diluting water from air, quite satisfactory results were obtained.

IV. RESULTS AND DISCUSSION

A. Preliminary Test of The Procedures (Run NB-1)

This run was the first with carbonate solutions. It was undertaken in the older stainless steel test system using aerated carbonate solutions containing no saline. Compositions are summarized in Table III. A major purpose of the run was to check the feasibility of operating in the mode planned for the new titanium test system with a minimum of deviations from earlier procedures. It also provided an opportunity to check out the equilibration tower for treatment of the feed solution with carbon dioxide containing gases as well as an opportunity to check the zirconia sensor's response to the carbonate buffer systems.

In this run two sensors, Y-1R and SP-6, were employed. The former was made with a commercial ceramic (composition 1372, yttria stabilized from Corning Glass Works) the latter with one that had been fabricated in house. The reference electrode, RD-5, had been used in previous experiments involving low salt concentrations.

The run extended over a period of five days. The sequence of conditions and the corresponding steady state potentials for the sensors vs. the reference electrode are summarized in Table IV. In connection with these potentials, it should be noted that during previous use the reference electrode had lost an indeterminate amount of the 0.1 m KCl with which it had originally been filled; the potentials therefore cannot be related in an absolute sense to any fixed potential scale. This is not important, however, since the equilibrations with acidic and basic solutions of known composition serve as calibration points in establishing response curves for the sensors; these are

Table III

CARBONATE SOLUTIONS EMPLOYED IN RUN NB-1

(Concentrations in Moles/1000g H_2O)

	Solution fed to tower		Equilibrating	Solution to Autoclave*			pH*at	
	$NaHCO_3$	Na_2CO_3	Gas	H_2CO_3	$NaHCO_3$	Na_2CO_3	25°	285°
A	4.70×10^{-2}	2.65×10^{-2}	Air (0.033% CO_2)	1.2×10^{-5}	4.6×10^{-2}	2.7×10^{-2}	9.8	9.5
B	4.70×10^{-2}	2.65×10^{-2}	100% CO_2	3.4×10^{-2}	1.0×10^{-1}	4.7×10^{-5}	6.7	8.3
C	1.0×10^{-3}	-	100% CO_2	3.4×10^{-2}	1.0×10^{-3}	3.5×10^{-9}	4.8	6.5

*Calculated with modified program from Reference 4.

Table IV

CONDITIONS AND STEADY STATE DATA FOR RUN NB-1

Condition No.	Time	Feed Stream	Measured Potentials vs. Reference @ 285°;mV		Ambient Temp. pH		
			Y-1R	SP-6	Calc'd.	In	Out
1	Day 1	0.0005m H_2SO_4	- 24	- 30	3.0	-	3.0
2	Day 1	0.001m NaOH	-530	-540	11.0	-	10.9
3	Day 2	0.0005m H_2SO_4	- 37	- 29	3.0	-	3.1
4	Day 3	Water	-210	-215	(5.8)*	-	(4.9)**
5	Day 3	Carb. Soln. A	-592	-593	9.8	9.7	9.9
6	Day 4	Carb. Soln. B	-582	-568	6.7	6.6	6.7
7	Day 5	Carb. Soln. C	-381	-371	4.8	4.8	5.2

*Value anticipated for water in equilibrium with the CO_2 in air

**Low because of incomplete flushing of previous acid from the system shown in Figure 3.

The pH values for the acidic and alkaline ''calibration'' solutions can be readily calculated and were taken from Reference 1. The pH values of the carbonate solutions were calculated using a program that is an extension of that previously described by Syrett, et al.(4); for a discussion of the program as well as a complete listing see Appendix A.

It is evident from the data in Table IV that the measured pH values at ambient temperature are in quite satisfactory agreement with the calculated values. For the higher temperature the pH values were obtained from the calibration curves in Figure 3. These values are summarized in Table V along with the calculated values. Again the agreement between the measured and the calculated values are considered satisfactory in view of the uncertainties in the calculated values, the possibility that some pH changes occurred through corrosion of the equipment, and uncertainties in the liquid junction potential between the reference electrode and the test solution. The excellent agreement between the measured values obtained with the two sensors is considered particularly encouraging.

B. Operation on Brines at 285°C (Runs GB-1 through GB-6)

This series of experiments was performed with a group of brines covering a variety of conditions including high and low salinity (20 and 0.2 percent NaCl), a range of pH (3.2 to 9.1 at 285°C) and a range of hydrogen sulfide concentrations (0.0 to 100 ppm). All of the conditions are listed in Table VI in which the indicated pH values were calculated using the program in Appendix A. Additional details regarding the compositions of the carbonate solutions are tabulated in Appendix B. For each run the solution employed during the ex-

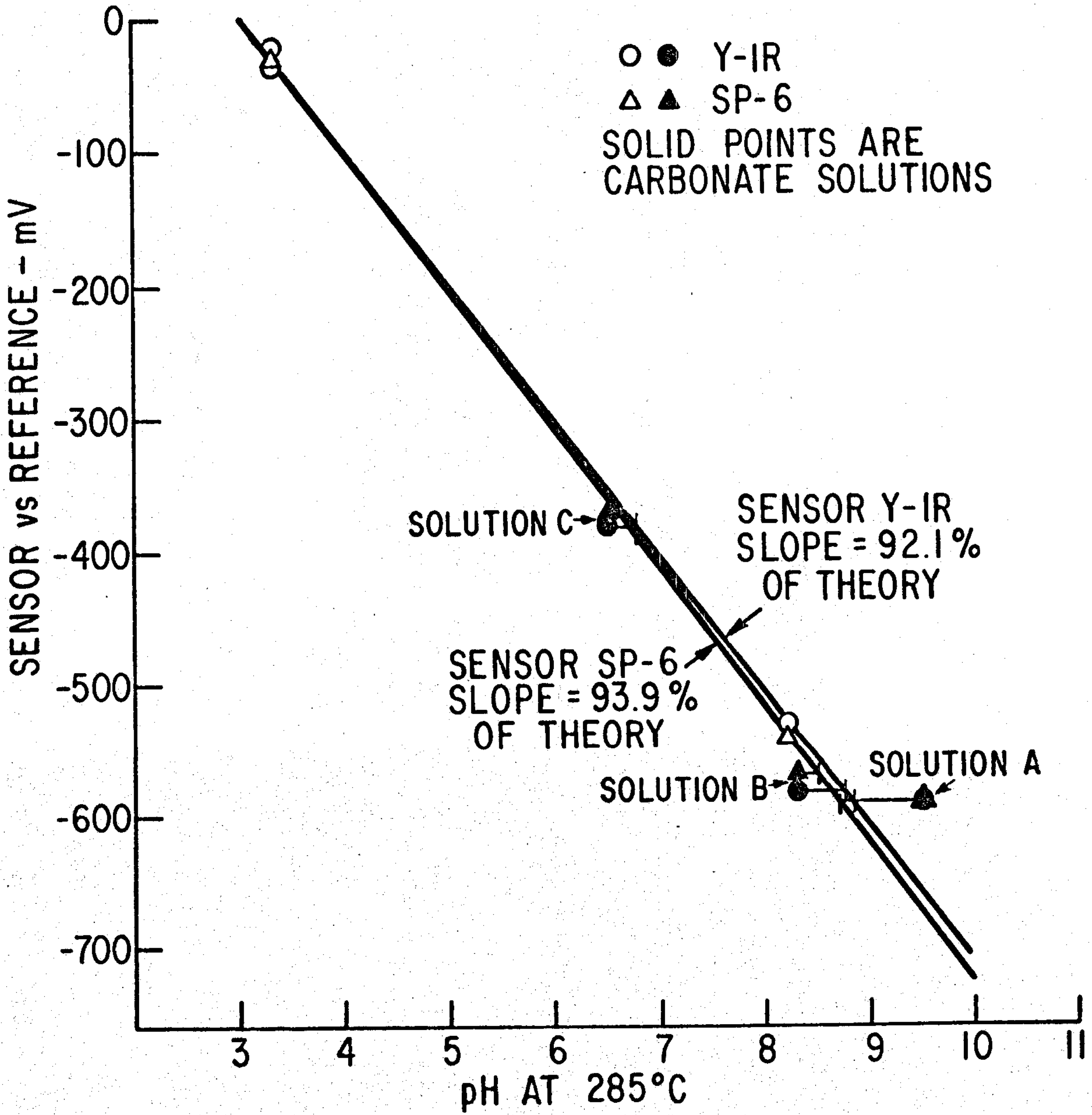

Figure 3. Calibration curves for sensors Y-IR and SP-6 at 285°C. (Run NB-1)

Table V

COMPARISON OF MEASURED AND CALCULATED VALUES OF pH at 285°C

Solution	Calculated pH	Measured Values			
		Sensor	Y-1R	Sensor	SP-6
		pH		pH	
A	9.5	8.8	−.07	8.7	−0.8
B	8.3	8.7	+0.4	8.5	+0.2
C	6.5	6.7	+0.2	6.6	+0.1

Table VI

COMPOSITIONS OF FEED SOLUTIONS USED IN RUNS GB-1 THROUGH 6

Run No.	Brine No.	[NaCl] m	Equivalent Base** m	[H_2S] ppm	Percent CO_2 in equilibrating gas	Calculated pH	
						25°C	285°C
GB-1	1A*	4.278 (20%)	0.109	–	1.0	8.6	8.6
	1B	4.278	0.109	–	100.0	6.6	7.8
GB-2	2A*	4.278	0.00109	–	100.0	4.6	5.8
GB-3	3A	4.278	(containing 0.001m HCl)		N_2	3.3	3.5
	3B	4.278	(containing 0.001m NaOH)		N_2	10.7	7.8
	3C(=1A)	4.278	0.109	–	1.0	8.6	8.6
	3Cs*	4.278	0.110	10	1.0	8.6	8.6
	3Ds	4.278	0.110	10	100.0	6.6	7.8
GB-4	4A(=2A)	4.278	0.00109	–	100.0	4.6	5.8
	4As*	4.278	0.00168	10	100.0	4.8	6.0
	4Bs	4.278	0.00168	10	1.0	6.8	7.3
GB-5	5As*	0.0342 (0.2%)	0.100	10	1.0	8.7	9.0
	5Bs	0.0342	0.100	10	100.0	6.7	8.2
GB-6	6A	0.0342	0.00100	–	100.0	4.8	6.4
	6As*	0.0342	0.00159	10	100.0	5.0	6.5
	6Bs*	0.0342	0.00159	10	1.0	6.9	7.9
	6Cs	0.0342	0.00688	100	100.0	5.6	7.1
	6Ds	0.0342	0.00688	100	1.0	7.4	8.2
	6E	0.0342	(containing 10^{-5}m HCl)		N_2	5.1	5.2
	6F	0.0342	(containing 10^{-4}m HCl)		N_2	4.1	4.2
	6G	0.0342	(containing 10^{-3}m HCl)		N_2	3.1	3.2
	6H	0.0342	(containing 10^{-4}m NaOH)		N_2	9.9	7.2
	6I	0.0342	(containing 10^{-3}m NaOH)		N_2	10.9	8.2

*Solution used for aging tests

**From added sodium bicarbonate and carbonate and the injected Na_2S

tended aging period is marked with an asterisk in Table VI. The other solutions were employed more briefly in order to obtain response data over a wide range of conditions. In general the sensors were exposed to the aging solution for periods from four to ten days but as will be noted one sensor was used for three successive runs and accumulated over 37 days exposure to a variety of conditions at 285°C.

Two reference electrodes and a platinum electrode to monitor the redox potential of the solution were employed in each run. With the exception of Run GB-6 one reference electrode in each case was freshly charged with a 0.1 m KCl electrolyte. As in Run NB-1 detailed potential measurements were made at various stages of each run.

Run GB-1 - This run, which was conducted in the new titanium system, was the first in which a simulated brine solution was employed. Deliberate effort was again made to tie this run to prior experience.

Virgin sensor Y-45 was employed along with two identical, newly fabricated reference electrodes, RD-9 and RD-10, both filled with 0.1 m KCl. Both reference electrodes had potentials of 97 mV against a commercial silver-silver chloride electrode containing 3.0 M KCl (Ingold) when immersed in 0.1 m KCl at 25°C. Their resistances measured under the same conditions were 3.0×10^5 and 2.2×10^5 ohms, respectively.

The run extended over a period of 11 days; conditions are summarized in Table VII. In greater detail, the system was brought to temperature with aerated water flowing through the autoclave. Initial calibration was accomplished with aerated sulfuric acid and sodium hydroxide. The system was then flushed with water which was subsequently deaerated. Additional calibrations

Table VII

CONDITIONS AND STEADY STATE DATA FOR RUN GB-1

Condition			Measured Potentials, mV at 25°C				Measured Potentials, mV at 285°C		
			Glass Electrode		Pt Electrode		Y-45	Pt	Ref RD-10
No.	Time	Feed Stream	In	Out	In	Out			
1	Day 1	Water*	**	123	**	492	−150	380	0
2	Day 1	0.0005 m H_2SO_4*		235		634	28	590	0
3	Day 1	0.001 m NaOH*		−234		100	−495	65	−5
4	Day 2	Water		85		292	−275	−510	0
5	Day 2	0.001 m HCl		235		431	70	−180	0
6	Day 2	0.001 m NaOH		−231		−302	−520	−709	−7
7	Day 3	0.001 m HCl		226		166	15	−170	−3
8	Day 3	0.001 m NaOH		−234		−668	−517	−677	+5
9	Day 4	Water		80		−254	−300	−430	0
10	Day 8	Brine 1A***	−117	−114	174	−701	−444	−678	+2
11	Day 8	Brine 1B	31	30	334	−505	−349	−577	+2
12	Day 10	Water		−138		−685	−284	−450	0
13	Day 10	0.001 m HCl		215		−311	105	−60	0
14	Day 10	0.001 m NaOH		−233		−810	−408	−650	0
15	Day 10	0.001 m HCl		228		−289	110	−15	5
16	Day 11	Water		−58		−601	−195	−375	−10

* These solutions were aerated; all others purged with N_2, N_2-CO_2 or CO_2

** In Run GB-1 the ambient condition glass-platinum electrode system was positioned where it could monitor only the brine solutions; this was changed for the later tests

***For brine compositions see Table VI and Appendix B.

were then undertaken with deaerated hydrochloric acid and sodium hydroxide. Upon observation that the potentials from the latter solutions were in satisfactory agreement with those from the former aerated solutions, operation was shifted to the brine equilibrated with one percent carbon dioxide in nitrogen. Operation on this solution was continued for 4 days. During this period a slow leak developed in a Swagelok seal on the primary reference electrode. It was therefore decided to truncate the run rather than to continue operation on the brine for seven days as originally planned.

Prior to termination, the brine was equilibrated with 100 percent carbon dioxide in order to introduce a pH change. About 4 hours were required before the potentials from the various monitoring points were on plateaus. The system was then flushed with water, and the following day transitions to 0.001 m hydrochloric acid and then to 0.001 m sodium hydroxide were undertaken in order to obtain new calibration points that could be compared with the starting values. Finally, the system was flushed with water and cooled.

Upon opening the autoclave and examining the sensor it was found to be sound and showed no visual signs of degradation. The two reference electrodes, however, did contain gas bubbles and their rest potentials could not be compared with their initial values against a commercial reference electrode.

Data collected during the run are included in Table VII. The pronounced potential changes that occurred at the platinum electrodes can be explained only by the introduction of reduced titanium species or hydrogen into the water through corrosion of the vessel. Analysis of the effluent stream for titanium indicated less than five parts per million. In addition, an occasional gas bubble was subsequently observed in the effluent stream. Although we did not collect and analyze a sample of the gas, we have done so under similar circumstances in the past and found it to be hydrogen. We therefore assume that under these conditions the platinum electrode actually serves as a hydrogen electrode and that the concentration of hydrogen in the water from corrosion of the system is fortuitously close to, but higher than, the saturation value under ambient conditions. In other words, with the aerated water oxygen reduction is the cathodic reaction accompanying corrosion of the system. At low oxygen concentrations, however, hydrogen evolution becomes the dominant cathodic reaction.

Potentials of the glass electrodes in the ambient temperature streams as well as those of the zirconia electrode as measured against their respective references are plotted as functions of time in Figure 4. Only data obtained with the acidic, alkaline and saline solutions are shown because considerable scatter was present with the unbuffered water.

Although very little drift occurred with the ambient temperature sensor throughout the run, some did occur with the zirconia electrode, at 285°C. This point is brought out more clearly by the data in Figure 5 which shows calibration curves at the start and finish of the run. Similar drift was observed at 285°C with the platinum (hydrogen) electrode.

The pH values for the brine solutions derived from the calibration curves in Figure 5 are summarized in Table VIII. Because of the drift and the fact that the data points were obtained closer to the final than the initial calibration, the high temperature pH values were determined on the basis of the final calibration curve for the zirconia sensor. The agreement between the

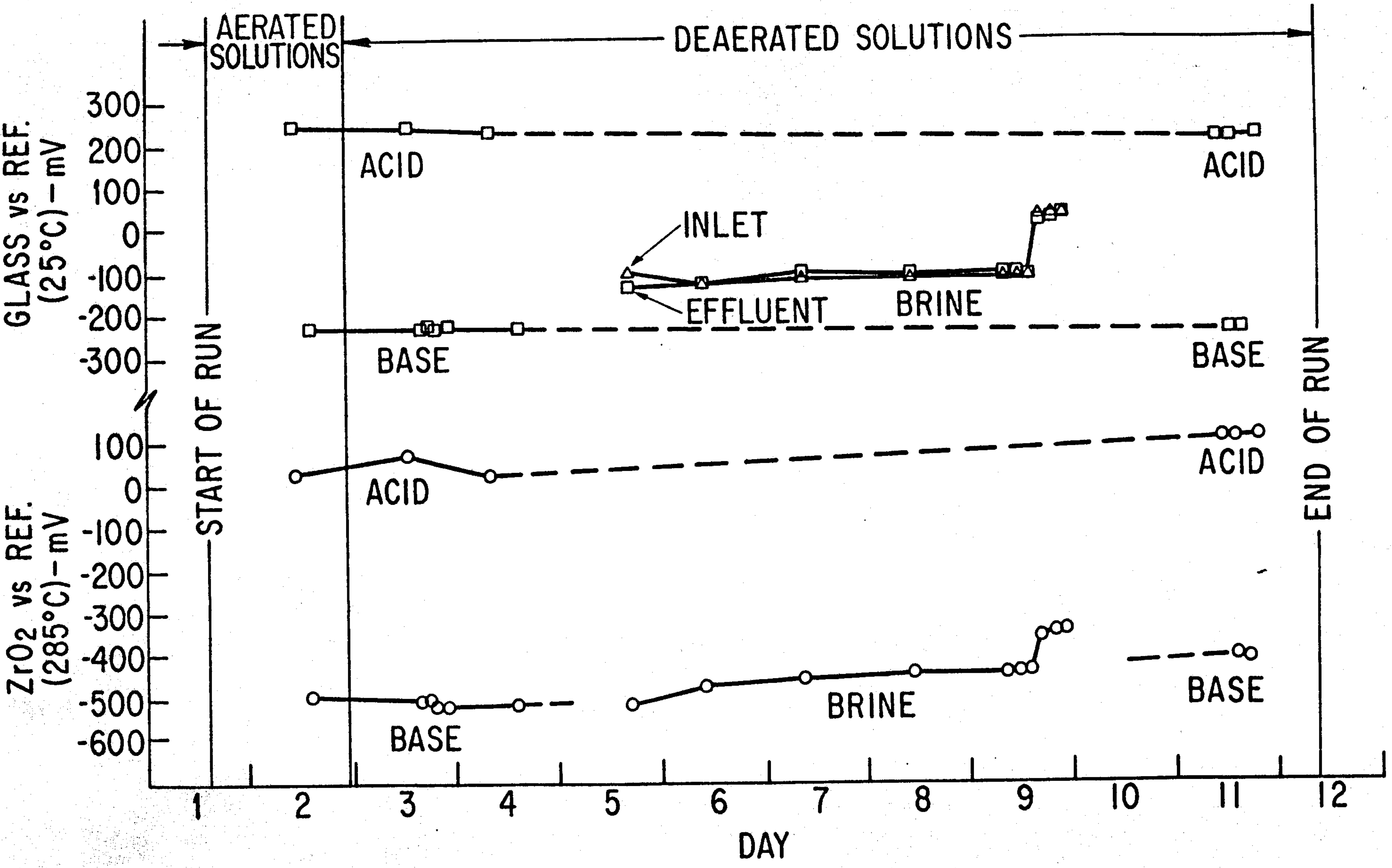

Figure 4. Potentials of zirconia sensor at 285°C and glass electrodes at 25°C vs. their respective reference electrodes during Run GB-1.

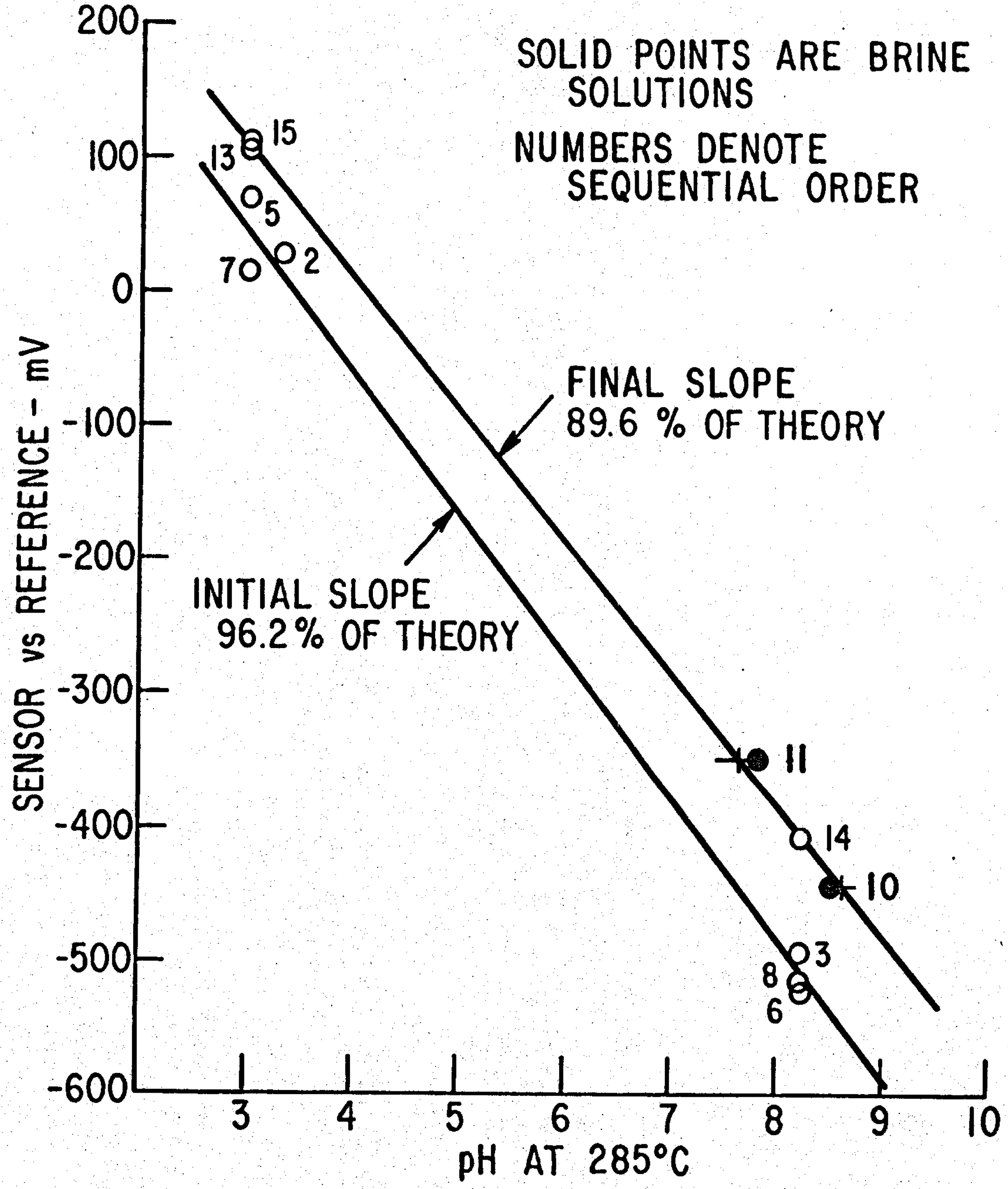

Figure 5. Calibration curves for zirconia sensor at 285°C. (Run GB-1)

Table VIII

COMPARISON OF MEASURED AND CALCULATED VALUES OF pH - RUN GB-1

Sensor Y-45; T = 285°C

Solution	pH		
	Calc.	Meas.	Δ
A	8.9	8.6	-0.3
B	8.3	7.6	-0.7

calculated and the measured values is similar to that observed in Run NB-1.

The drift in the calibration curve with time is a phenomenon that we have encountered previously.(2) It appears to be associated with changes in the internal chloride concentration in the reference electrode. Because such drift was not reported in the original description of the electrode,(3) it may reflect our omission of the internal zirconia thread from the structure. Such a thread might reduce convection in the internal electrolyte and thereby improve stability. Alternatively our zirconia junction might have been more porous than that used previously.

Run GB-2 - Sensor Y-45 and reference electrode RD-10 from Run GB-1 were reused in this run. A second reference electrode RD-9R had also been used in the previous run, but it was refilled with fresh 0.1 m KCl prior to reuse; it served as the primary reference against which all other measurements were made. The brine was similar to that of Run GB-1 except for a lower bicarbonate concentration.

Conditions and performance data at various stages of the run, which extended over a period of six days, are summarized in Table IX. Potentials of the glass electrodes in the ambient temperature streams as well as those of the zirconia electrode as measured against their respective references are plotted against time in Figure 6. Together these sets of data provide a condensed history of the run.

In greater detail, the system was brought to temperature with deaerated water flowing through the autoclave. Calibration of the sensor-reference electrode combination was then undertaken with deaerated hydrochloric acid and sodium hydroxide. Operation was then shifted to the brine equilibrated with

Table IX

CONDITIONS AND STEADY STATE DATA FOR RUN GB-2

Condition No.	Time	Feed Stream	Measured Potentials, mV at 25°C Glass Electrode In	Out	Pt Electrode In	Out	Measured Potentials, mV at 285°C Y-45	Pt	Ref RD-10
1	Day 2	Water*	92	52	365	-505	-240	-213	-30
2	Day 2	0.001 m HCl	228	239	555	12	60	307	-40
3	Day 2	0.001 m NaOH	-237	-230	52	-683	-470	-645	-40
4	Day 7	Brine A**	147	142	408	-316	-529	-433	0

*All solutions were purged with N_2 except Brine A, which was equilibrated with CO_2.

**For brine composition see Table VI and Appendix B.

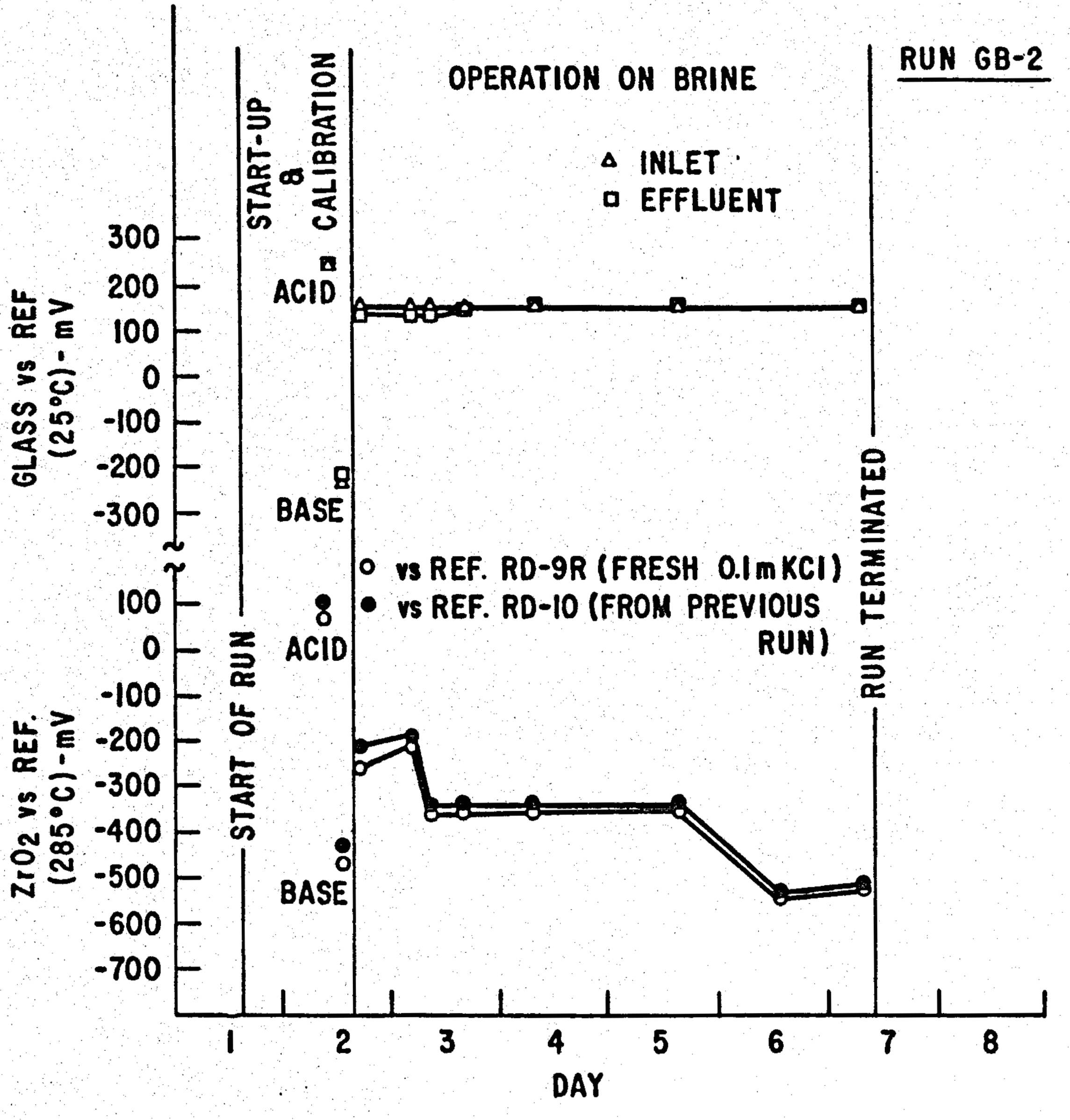

Figure 6. Potentials of zirconia sensor at 285°C and glass electrodes at 25°C vs. their respective reference electrodes during Run GB-2.

pure carbon dioxide. From Figure 6 it is clear that the high temperature measurements were much less stable than the low during this period. On the fifth day of operation with the brine, the resistance measured between the zirconia sensor and the reference electrode or the platinum electrode was low, indicating that the sensor had failed. The run was therefore terminated at this point. Upon removing the sensor from the autoclave it was found to have cracked within the pressure fitting. It is likely that this occurred because of too limited a clearance between the ceramic tube and the steel wall of the fitting. In subsequent sensors discussed in this report greater clearance was provided.

It is of interest to note that at the start of the tests reference electrode RD-10 was about 40 mV negative with respect to RD-9R, indicative of a higher chloride ion concentration in the former. At termination the difference had fallen to essentially zero. Presumably this reflects the entry of brine into reference RD-9R. Reference RD-10 had already been exposed to brine in the previous run.

Run GB-3 - Rather than repeat run GB-2 it was elected to proceed to the next scheduled run in order to gain experience with a sulfide-containing brine. This run was similar to GB-1 except for the addition of the sulfide (condition 3 in Table II). Because of the failure of sensor Y-45 in the previous run, a new sensor Y-47 was employed. The two reference electrodes were also new; RD-13 was filled with 0.1 m KCl and RD-14 with a 20 weight percent NaCl solution.

In this run 0.00075 m HCl and 0.0005 m NaOH were inadvertently used for the initial calibration in place of the usual one millimolal reagents. Following this operation two additional steps were introduced when the system was operated briefly with Brines 3A and B containing 0.00109 m HCl and NaOH, respectively, both in twenty per cent NaCl. This was followed by the transition to the carbonate buffered brine solution equilibrated with 1 per cent CO_2 in N_2. After a day's operation on the simple brine, sulfide injection was started to maintain the level at about 10 ppm for a period of 7 days. No detectable change occurred in the output of the pH sensor upon the addition of the sulfide. At the conclusion of this aging period a pH change was induced by equilibrating the brine with carbon dioxide while retaining the sulfide concentration at 10 ppm. Finally the sensor was recalibrated with acid and base after flushing the brine from the system with water.

The complete run extended over a period of 11 days. Conditions and steady state performance data at various stages are summarized in Table X, and potentials of the ambient and high temperature pH sensors vs. their respective reference electrodes are plotted against time in Figure 7. During operation on the sulfide, analyses of the stock solution and the effluent were performed with the results in Table XI. Since input conditions were adjusted for 11 ppm in the feed to the autoclave, a small loss on passage through the system seems to have occurred. This is undoubtedly real and probably reflects reaction with metal and corrosion products in the system.

As in Run GB-2 the potentials of the two non-identical reference electrodes were found to converge during the run. Initially the electrode containing twenty percent NaCl was 40-50 mV negative to that containing the 0.1 m KCl. At the end of the run this difference had fallen through zero and was slightly positive. Upon draining the filling solutions from the two, the analyses in Table XII were obtained. Clearly the concentrations had converged

Table X

CONDITIONS AND STEADY STATE DATA FOR RUN GB-3

			Measured Potentials, mV at 25°C				Measured Potentials, mV at 285°C		
			Glass Electrode		Pt Electrode		Y-47	Pt	Ref RD-14
Condition No.	Time	Feed Stream	In	Out	In	Out			
1	Day 2	Water*	36	110	——	——	-207	-406	-35
2	2	0.00075 m HCl	242	229	555	93	45	-9	-58
3	2	0.0005 m NaOH	-167	-212	155	-543	-438	-630	-20
4	3	Brine 3A**	-273	224	612	-396	-54	-344	-47
5	3	Brine 3B	-214	-209	126	-814	-354	-612	-41
6	4	Brine 3C	-106	-103	205	-724	-447	-758	-26
7	5	Brine 3Cs	-105	-101	-493	-724	-442	-760	-20
8	11	Brine 3Cs	-102	-104	-468	-664	-436	-731	-7
9	11	Brine 3Ds	50	26	-494	-599	-356	-616	-6
10	12	Water	131	-94	278	-589	-313	-502	-8
11	12	0.001 m HCl	236	218	322	-352	91	-120	9
12	12	0.001 m NaOH	-195	-228	1	-658	-430	-614	12
13	12	0.001 m HCl	237	228	384	-246	107	-62	12

*All solutions were purged with N_2, N_2-CO_2 or CO_2.

**For brine compositions see Table VI and Appendix B.

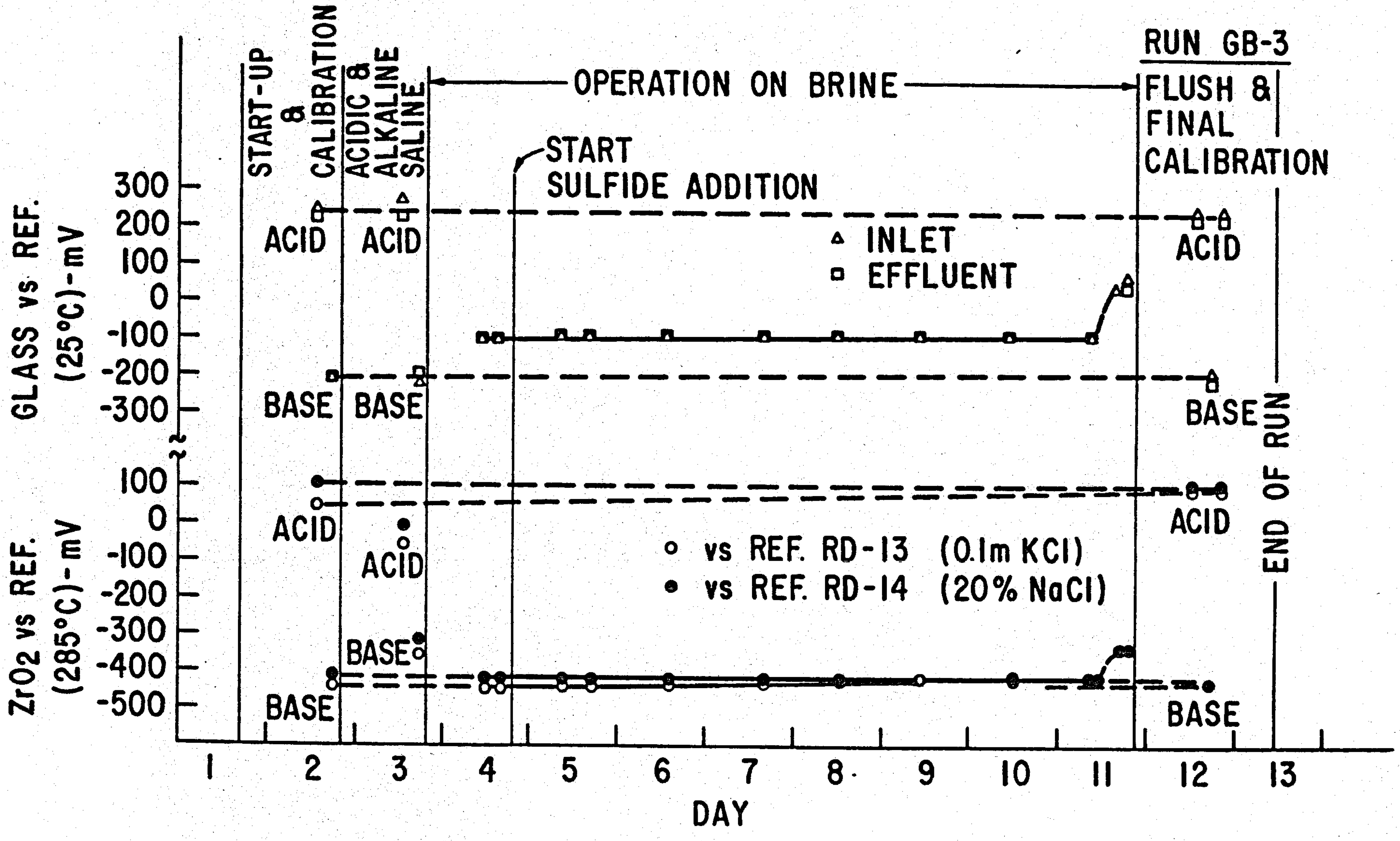

Figure 7. Potentials of zirconia sensor at 285°C and glass electrodes at 25°C vs. their respective reference electrodes during Run GB-3.

Table XI

SULFIDE ANALYSES OF STOCK SOLUTION AND EFFLUENT

Day of Run	Brine	Stock Solution*	Effluent
5	Cs	1162	9.3
9	Cs	1040	7.3
11	Cs		8.3
11	Ds		7.7

*Nominally 1200 ppm. At the flow ratios employed, 1200 ppm in the stock solution would give 11 ppm in the feed to autoclave.

Table XII

ANALYSES OF INTERNAL SOLUTIONS IN REFERENCE ELECTRODES FOR RUN GB-3

REFERENCE	INITIAL SOLUTION	SOLUTION AT END OF RUN		
		$[K^+]$	$[Na^+]$	$[Cl^-]$
RD-13	0.10 m KCL	0.03 m	1.4 m	1.5 m
RD-14	4.28 m NaCl (20w/o)	----	1.5	1.8

during exposure to the brine. It would appear, however, that considerable redilution must have occurred during the last day or so of operation on the calibrating solutions and the water and during cool-down.

Turning now to a consideration of the pH values obtained for the various brines with the high temperature sensor, we shall first consider those of the solutions containing HCl and NaOH. The potentials of the sensor vs. both reference electrodes are noted in Figure 8 which contains calibration curves for the sensor vs. each reference electrode at the start of the run. The pH values calculated for the two solutions using the computer program in Appendix A were used in placing the solid points on Figure 8. It is evident that the calculated pH values deviate moderately from the pH values read from the intercepts of the potentials with the calibration curves. These deviations are expressed numerically in Table XIII. Also indicated in Table XIII are the activity coefficients one calculates for the hydrogen and hydroxide ions based upon the measured pH values and the concentrations of acid and base added to the brines. These are to be compared with a value of 0.288 calculated with the computer program.

Now turning to Figure 9 we see a single calibration curve for the sensor vs. either reference electrode at the end of the run. (To indicate the extent of drift, initial calibration curves are also shown as broken lines.) Using the final calibration curve we can estimate the pH values of the brine solutions containing carbon dioxide and the dissociation products of carbonic acid. These values along with the calculated values are included in Table XIII. It is of interest to note that the deviations between measured and calculated values are similar to those observed with the brines containing HCl and NaOH.

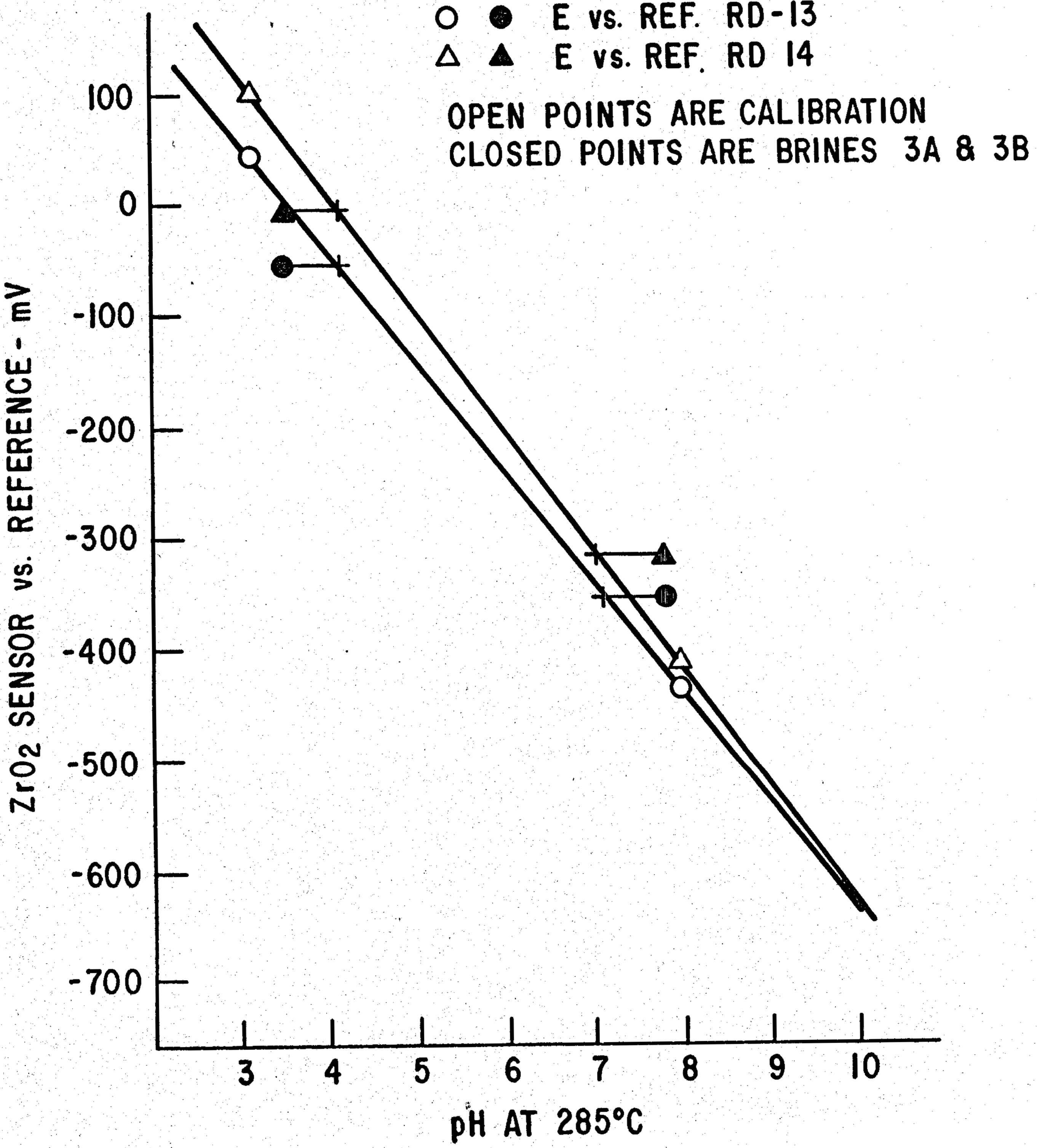

Figure 8. Initial calibration curves for zirconia sensor vs. two reference electrodes at 285°C. Solid points were obtained with brines containing HCl and NaOH (Run GB-3).

Table XIII

COMPARISON OF MEASURED AND CALCULATED VALUES OF pH AT 285°C

SOLUTION	CALCULATED	MEASURED	Δ	$\gamma_{H^+}(\gamma_{OH^-})$* Calc. from Measured pH
A	3.5	4.1	+0.6	0.079
B	7.8	7.1	−0.7	0.057
Cs	8.6	8.2	−0.4	----
Ds	7.8	7.4	−0.4	----

*$\gamma_{H^+} = a_{H^+}/C_{H^+} = 10^{-pH}/C_{H^+}$

$\gamma_{OH^-} = K_w/(a_{H^+} \cdot C_{OH^-}) = K_w/(10^{-pH} \cdot C_{OH^-})$

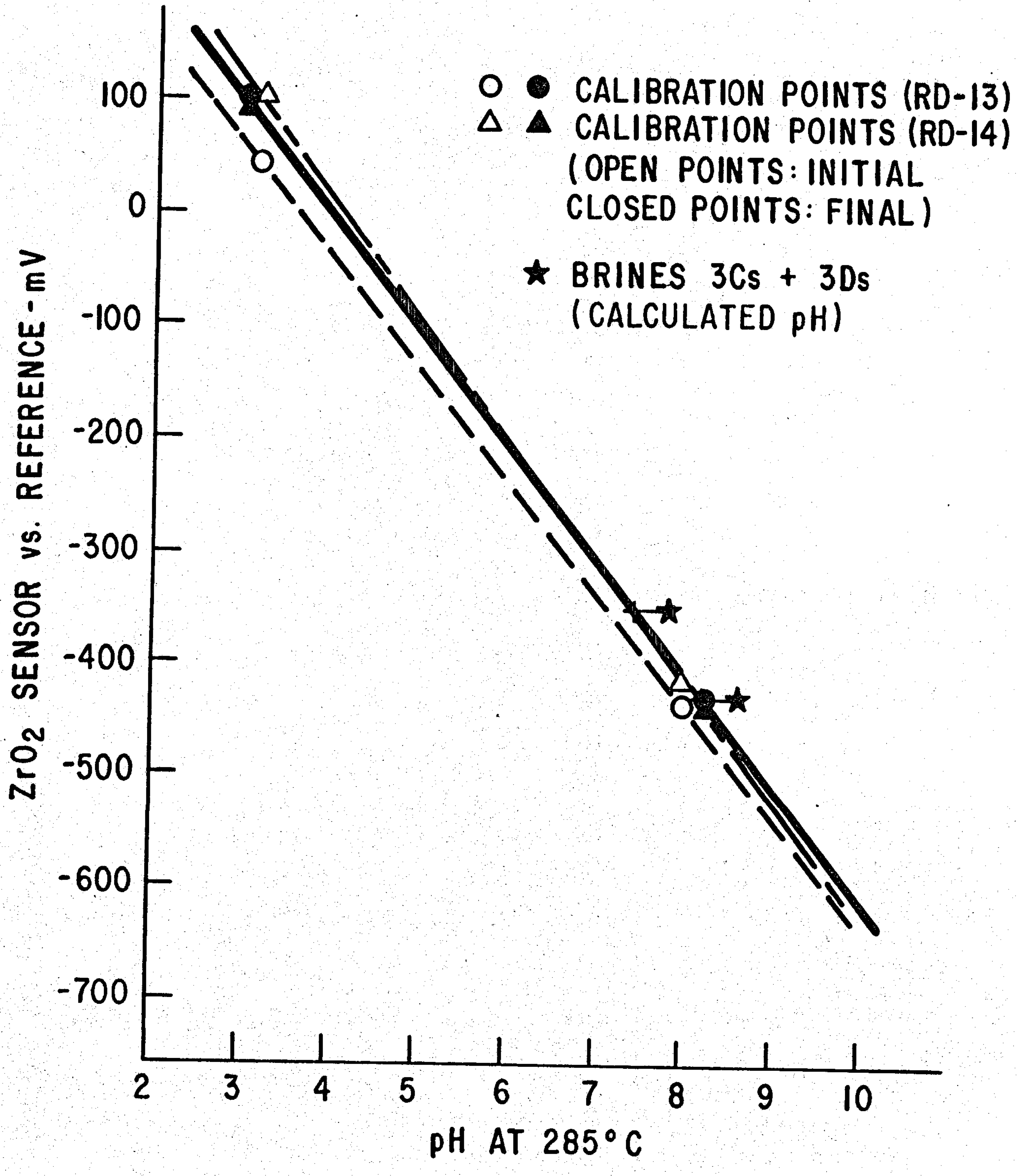

Figure 9. Calibration curves for zirconia sensor at 285°C showing data points for carbonate buffered brines. (Run GB-3).

It is suggested that the observed deviations result more from a failure of the computer program to properly estimate activity coefficients of the trace constituents of the brine solutions than from shortcomings in the measurements with the sensor-reference electrode combination. This suggestion is supported by experience with mixed electrolytes at lower temperatures.(6,7) Much available data indicates that the activity coefficients of ''trace'' constituents differ markedly from those of macro constituents in mixed electrolytes. The model of Syrett, et al. from which the present computer program was derived assumes that all are the same.

Run GB-4 - This run was similar to GB-3 except that the brine used for aging was more acidic. A new sensor Y-48 was employed along with two new reference electrodes, one containing 0.1 m KCl, the other 3.0 m KCl. About 10 ppm of hydrogen sulfide was added to the brines from the start. Aging on the more acidic brine extended over a period of seven days. Summary data are recorded in Table XIV and Figure 10, and calibration curves are shown in Figure 11. Again some drift was evident, but, as expected, this was greater with the 0.1 m KCl reference electrode than with the more concentrated. A comparison of measured and calculated pH values is given in Table XV.

Run GB-5 - This run differed from the previous four in that the brine concentration was at the 0.2 per cent level. The hydrogen sulfide concentration was maintained at the 10 ppm level. Sensor Y-48 was continued in use from the previous run, but new reference electrodes containing 0.1 m KCl and 0.2 per cent NaCl solutions were employed. Aging was performed in the more alkaline brine for a period of about ten days.

In contrast to the earlier runs the drift in potentials with time was to-

Table XIV

CONDITIONS AND STEADY STATE DATA FOR RUN GB-4

			Measured Potentials, mV at 25°C				Measured Potentials, mV at 285°C				
Condition	Time		Glass Electrode		Pt Electrode		Y-48		Pt		Ref. B*
No.	(Day)	Feed Stream	In	Out	In	Out	vs A*	vs B*	vs A*	vs B*	vs A*
1	2	Water	126	112	358	117	-275	-280	-395	-320	-75
2	2	0.001 m HCl	231	244	420	163	+13	75	-89	-25	-62
3	2	0.001 m NaOH	-186	-225	72	-90	-520	-460	-670	-610	-60
4	3	Brine 4A**	147	145	292	9	-234	-183	-355	-304	-51
5a	3	Brine 4As	132	138	-	-395	-233	-191	-400	-358	-42
5b	4	"	100	130	-315	-372	-230	-207	-412	-389	-23
5c	5	"	121	135	-307	-358	-206	-192	-392	-378	-14
5d	6	"	134	137	-303	-348	-193	-183	-382	-372	-10
5e	6	"	142	135	-328	-351	-193	-184	-384	-375	-9
5f	7	"	130	135	-321	-351	-187	-180	-378	-371	-7
5g	8	"	103	127	-354	-351	-197	-191	-395	-389	-6
5h	8	"	104	126	-348	-351	-197	-192	-396	-391	-5
5i	9	"	105	126	-343	-352	-196	-192	-396	-392	-4
5j	10	"	149	138	-285	-341	-198	-194	-369	-365	-4
6	10	Brine 4Bs	-37	-36	-451	-498	-298	-293	-488	-483	-5
7	11	Water	"	"	"	"	-156	-148	-339	-331	-8
8	11	0.001 m HCl	a	239	a	a	+116	+116	-32	-32	0
9	11	0.001 m NaOH	a	-230	a	a	-445	-438	-569	-562	-7
10	12	Water	a	116	a	a	-159	-149	-369	-359	-10

*A = Ref RD-13R initially containing 0.1 m KCl

B = Ref RD-14R initially containing 3.0 m KCl

**For brine compositions see Table VI and Appendix B

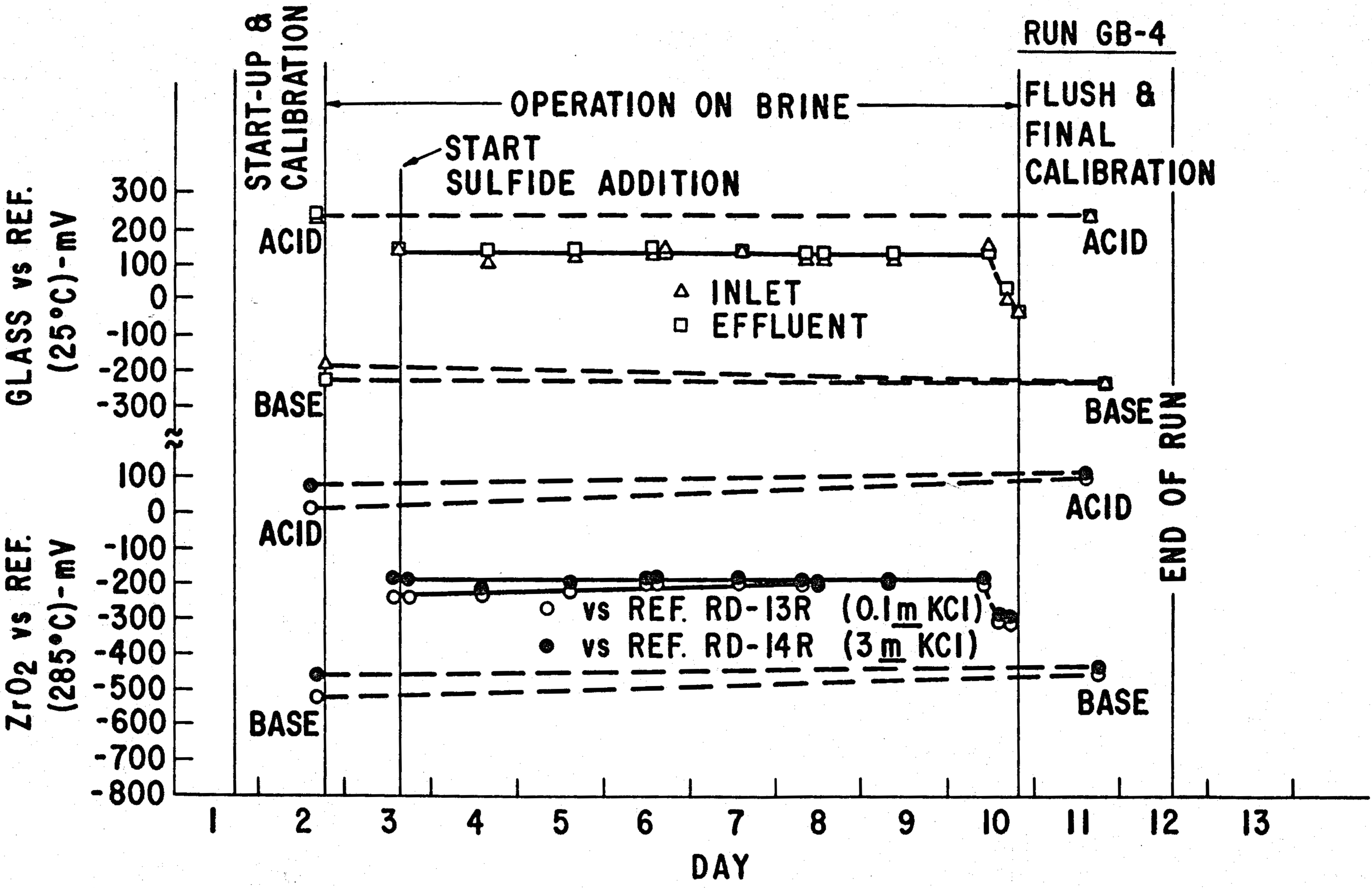

Figure 10. Potentials of zirconia sensor at 285°C and glass electrodes at 25°C vs. their respective reference electrodes during Run GB-4.

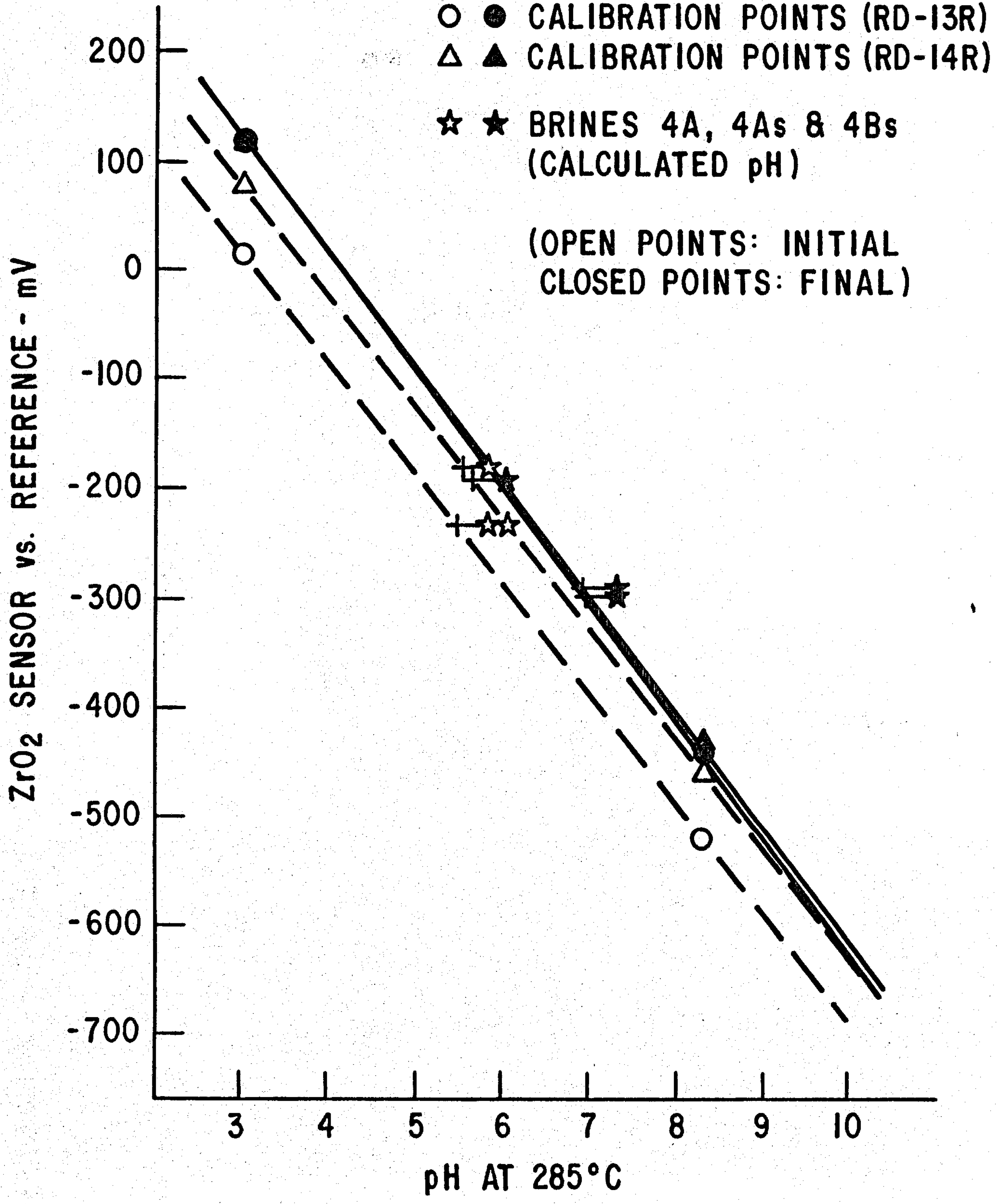

Figure 11. Calibration curves for zirconia sensor at 285°C showing data points for carbonate-buffered brines. (Run GB-4).

Table XV

COMPARISON OF MEASURED AND CALCULATED VALUES OF pH AT 285°C - RUN GB-4

Day of Measurement	Solution	Calculated pH	Measured pH vs Ref 13R	Measured pH vs Ref 14R	Measured pH Mean	ΔpH Mean-Calcd.
3	4A	5.84	5.48*	5.58*	5.53	−0.31
3	4As	6.02	5.47*	5.66*	5.56	−.46
10	"	"	5.99	5.99	5.99	−.03
10	4Bs	7.33	6.93	6.93	6.93	−.40

*Derived from initial calibration curve; others from final.

wards lower values rather than higher. This is to be expected for the 0.1 m KCl reference because chloride should be lost to the more dilute brine solution being monitored. It would be expected that the output of the sensor vs. the 0.2 per cent NaCl reference would have remained constant, but some drift did occur in this case as well. The summary data are recorded in Table XVI and Figure 12, and calibration curves are shown in Figure 13. Summaries of the calculated and measured pH values are found in Table XVII.

Run GB-6 - This run was carried out as a continuation of the previous one without changing the sensor or the reference electrodes. Only the brine was changed to one of more acidic character by lowering the equivalent base concentration from 0.1 to 0.001 m. Conditions are summarized in Table XVIII and Figure 14, and a calibration curve appears in Figure 15. After about seven days operation on the brines containing 10 ppm hydrogen sulfide, the level was raised to 100 ppm for two days. This had no apparent effect apart from that associated with the pH change resulting from the introduction of an increased amount of equivalent base in the form of the sodium sulfide. Later in the run the sensor was exposed successively to 0.2 per cent brine solutions 6E through 6I containing different levels of free hydrochloric acid and sodium hydroxide. Operation was straightforward throughout and the sensor remained in excellent condition after 37 days of almost continuous operation through three consecutive runs. The pH data relating to this run are summarized in Table XIX. They were derived on the basis of the same calibration curve as the final one for Run GB-5.

General - It has been evident above that quite satisfactory agreement has been seen between measured and calculated pH values in the individual runs. The accumulated data from the several individual experiments are combined and

Table XVI

CONDITIONS AND STEADY STATE DATA FOR RUN GB-5

			Measured Potentials, mV at 25°C				Measured Potentials, mV at 285°C				
Condition	Time		Glass Electrode		Pt Electrode		Y-48		Pt		Ref. B*
No.	(Day)	Feed Stream	In	Out	In	Out	vs A*	vs B*	vs A*	vs B*	vs A*
1	2	Water	158	134	326	420	-173	-193	398	378	20
2	2	0.001 m HCl	236	236	405	353	36	19	424	407	17
3	2	0.001 m NaOH	-217	-222	21	-70	-480	-510	-172	-202	30
4a	3	Brine 5As**	-165	-163	50	-600	-625	-654	-952	-970	29
4b	5	"	-161	-161	75	-780	-630	-658	-950	-978	28
4c	7	"	-155	-155	-	-	-627	-655	-960	-988	28
4d	9	"	-149	-152	-441	-756	-640	-661	-956	-977	21
4e	10	"	-158	-157	-439	-763	-648	-666	-967	-985	18
4f	11	"	-158	-159	-445	-764	-650	-667	-970	-987	17
4g	12	"	-157	159	-452	-764	-652	666	-972	-986	14
5	12	Brine 5Bs	12	6	-344	-541	-573	-587	-762	-776	14
6	13	Water	125	115	214	-358	-410	-430	-475	-495	20
7	13	0.001 m HCl	229	231	285	281	-20	8	-109	-81	-28
8	13	0.001 m NaOH	-217	-221	-51	-705	-556	-530	-590	-564	-26

*A = Ref RD-13RR initially containing 0.1 m KCl

B = Ref RD-14RR initially containing 0.2 percent NaCl

**For brine compositions see Table VI and Appendix B

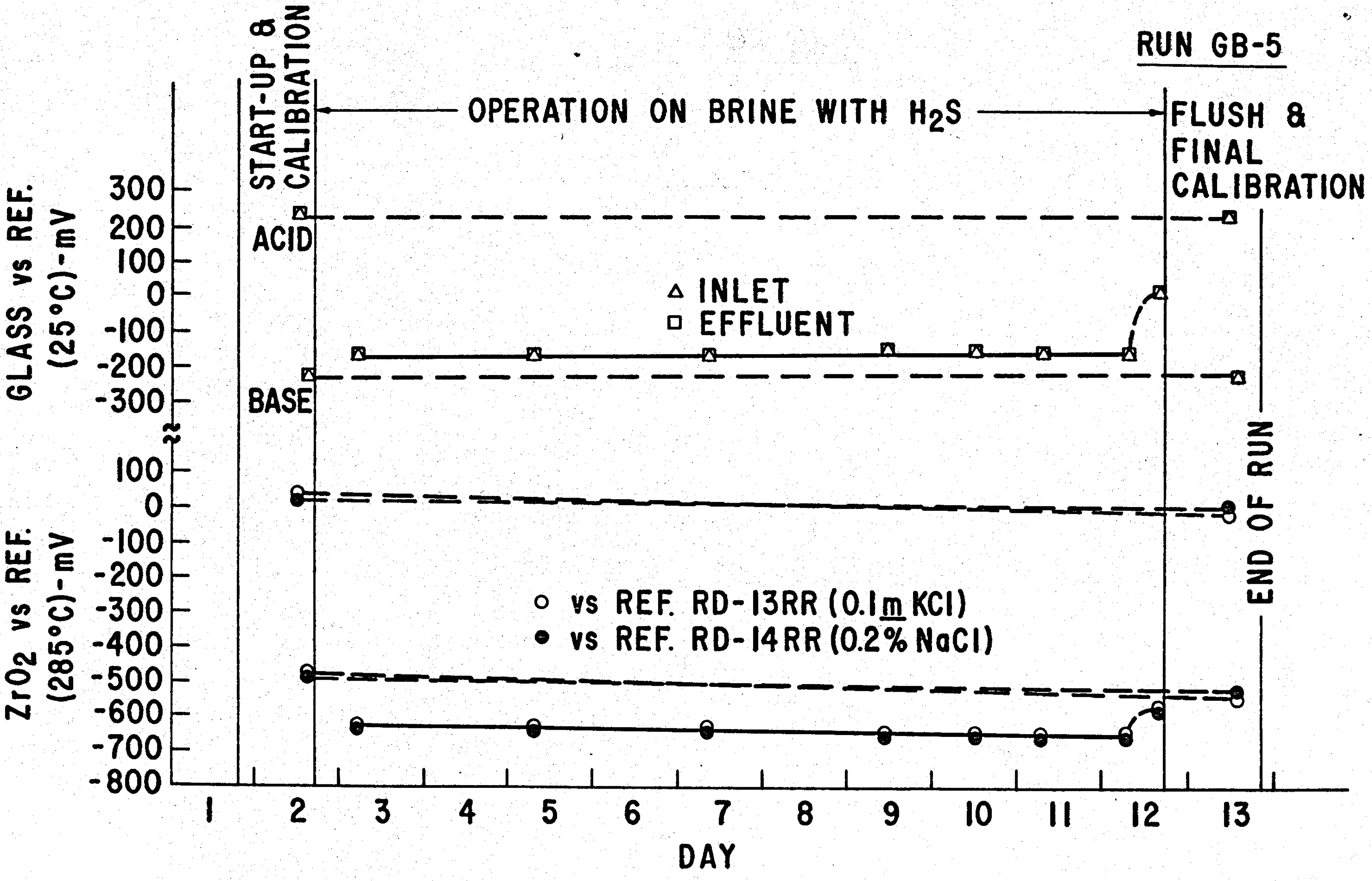

Figure 12. Potentials of zirconia sensor at 285°C and glass electrodes at 25°C vs. their respective reference electrodes during Run GB-5.

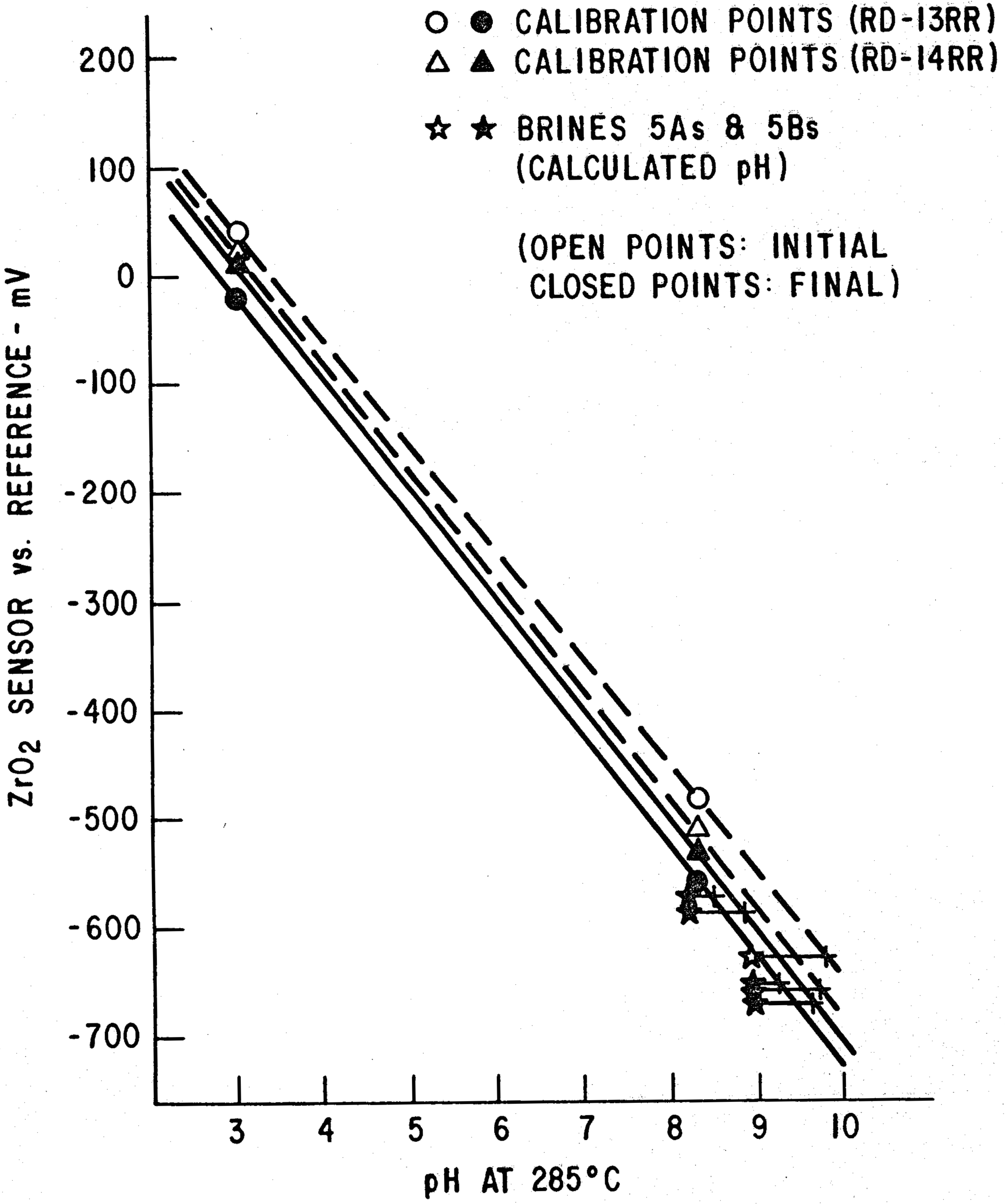

Figure 13. Calibration curves for zirconia sensor at 285°C showing data points for carbonate-buffered brines. (Run GB-5).

Table XVII

COMPARISON OF MEASURED AND CALCULATED VALUES OF pH AT 285°C - RUN GB-5

Day of Measurement	Solution	Calculated pH	Measured pH vs Ref 13RR	Measured pH vs Ref 14RR	Mean	ΔpH Mean-Calcd.
3	Brine 5As	8.99	9.79*	9.74*	9.76	0.77
12	"	8.99	9.25	9.64	9.44	.45
12	Brine 5Bs	8.23	8.48	8.87	8.68	.45

*Derived from initial calibration curves; others from final.

Table XVIII

CONDITIONS AND STEADY STATE DATA FOR RUN GB-6

			Measured Potentials, mV at 25°C				Measured Potentials, mV at 285°C				
Condition	Time		Glass Electrode		Pt Electrode		Y-48		Pt		Ref. B*
No.	(Day)	Feed Stream	In	Out	In	Out	vs A*	vs B*	vs A*	vs B*	vs A*
1	1	Water	125	115	214	-358	-410	-430	-475	-495	20
2	1	0.001 m HCl	229	231	285	-281	-20	+8	-109	-81	-28
3	1	0.001 m NaOH	-217	-24	-51	-705	-556	-530	-590	-564	-26
4a	2	Brine 6A**	126	122	258	-271	-367	-380	-494	-507	+13
4b	2	"	126	122	233	-258	-369	-382	-494	-507	+13
4c	2	"	127	122	255	-231	-370	-382	-493	-505	+12
5a	3	Brine 6As	121	114	-223	-360	-387	-399	-585	-597	+12
5b	3	"	129	114	-217	-357	-388	-399	-582	-593	+11
5c	4	"	122	116	-257	-338	-386	-396	-574	-584	+10
5d	4	"	122	115	-261	-337	-390	-398	-576	-584	+8
6a	5	Brine 6Bs	-80	-52	-430	-489	-520	-507	-710	-697	-13
6b	6	"	-86	-65	-432	-488	-522	-509	-714	-701	-13
7a	7	Brine 6As	74	115	-293	-313	-400	-393	-589	-582	-7
7b	8	"	130	116	-184	-303	-397	-389	-580	-572	-8
7c	9	"	122	117	-258	-295	-397	-388	-580	-571	-9
7d	9	"	131	117	-161	-296	-400	-391	-584	-575	-9
8a	9	Brine 6Cs	89	82	-350	-335	-462	-451	-665	-654	-11
8b	10	"	99	75	-345	-335	-468	-460	-673	-665	-8
9a	11	Brine 6Ds	-220	-230	-561	-583	-594	-585	-790	-781	-9
9b	11	"	-222	-248	-561	-583	-594	-585	-803	-794	-9
10a	12	Brine 6E	89	-35	134	-340	-295	-271	-449	-425	-24
10b	14	"	94	+35	171	-269	-293	-276	-478	-461	-17
10c	14	"	93	52	172	-248	-295	-277	-456	-438	-18
11a	14	Brine 6F	168	164	182	-65	-107	-99	-262	-254	-8
11b	15	"	168	170	186	37	-105	-89	-253	-237	-16
12a	15	Brine 6G	230	232	192	116	14	29	-130	-115	-15
13a	16	Brine 6H	-146	-140	-23	-161	-425	-413	-576	-564	-12
13b	16	"	-142	-142	-35	-168	-428	-414	-576	-562	-14
14	16	Brine 6I	-224	-223	-51	-240	-541	-525	-678	-662	-16

*A = Ref RD-13RR from Run GB-5

B = Ref RD-14RR from Run GB-5

**For brine compositions see Table VI and Appendix B

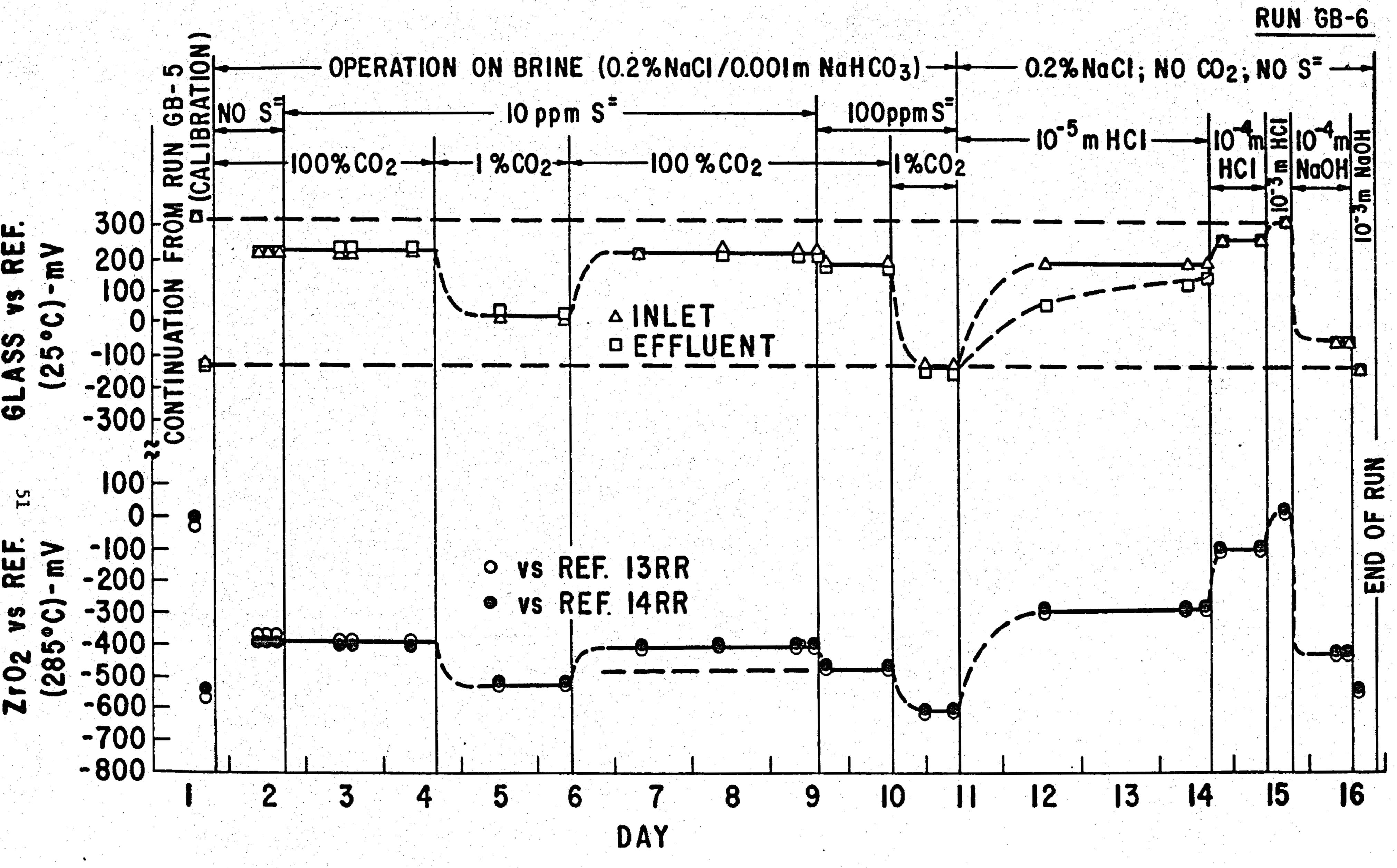

Figure 14. Potentials of zirconia sensor at 285°C and glass electrodes at 25°C vs. their respective reference electrodes during Run GB-6.

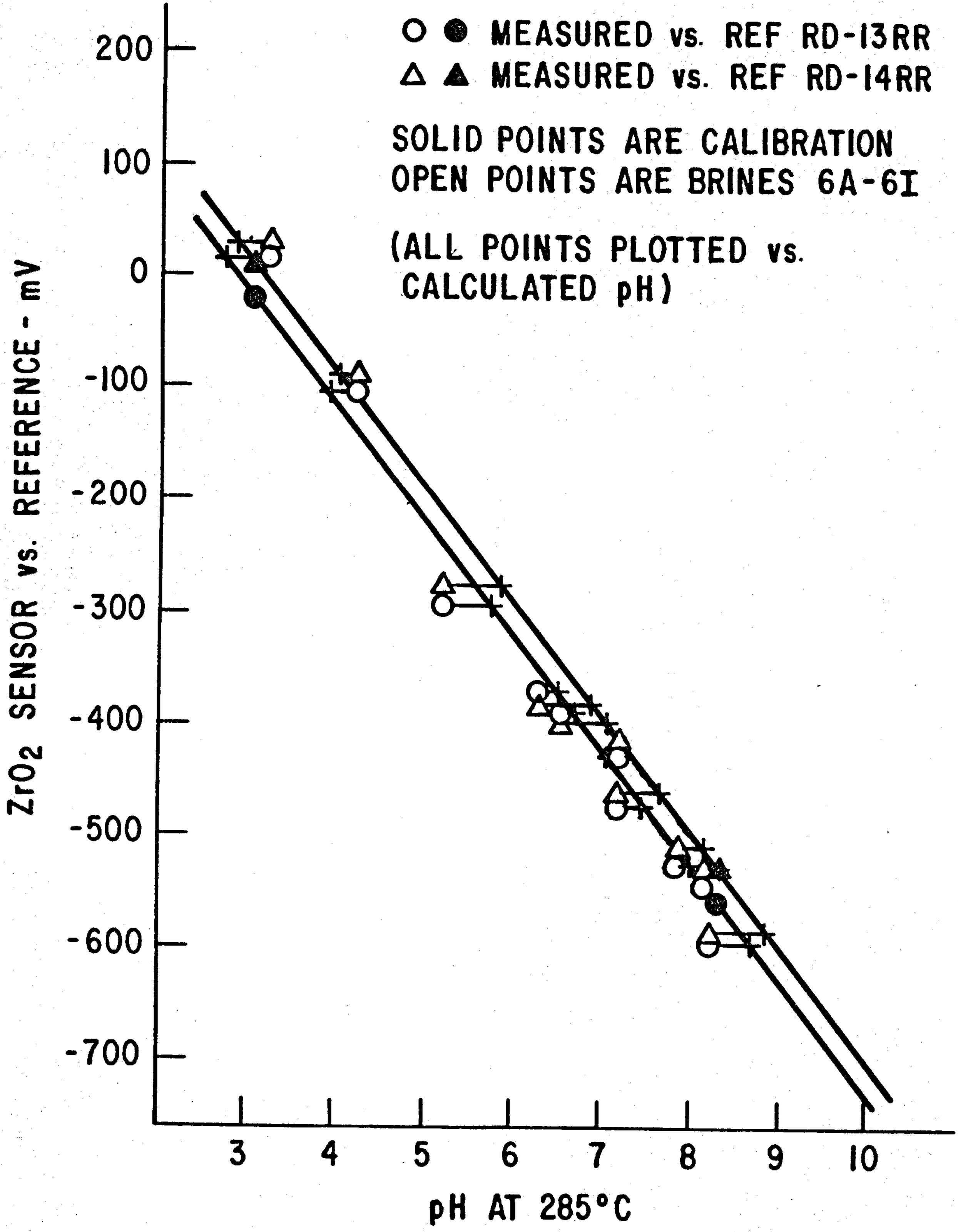

Figure 15. Calibration curves for zirconia sensor at 285°C showing data points for carbonate-buffered brines. (Run GB-6).

Table XIX

COMPARISON OF MEASURED AND CALCULATED VALUES OF pH AT 285°C - RUN GB-6

Day of Measurement	Solution	Calculated pH	Measured pH			ΔpH
			vs Ref 13RR	vs Ref 14RR	Mean	Mean-Calcd.
2	Brine 6A	6.35	6.48*	6.86*	6.67	0.32
4	Brine 6As	6.54	6.68	7.02	6.85	0.31
6	Brine 6Bs	7.89	7.97	8.10	8.04	.15
9	Brine 6As	6.54	6.78	6.95	6.86	.32
10	Brine 6Cs	7.14	7.44	7.62	7.53	.39
11	Brine 6Ds	8.25	8.68	8.85	8.76	.51
14	Brine 6E	5.19	5.74	5.83	5.78	.59
15	Brine 6F	4.19	3.88	3.99	3.94	-.25
15	Brine 6G	3.19	2.71	2.84	2.78	-.41
16	Brine 6H	7.16	7.05	7.17	7.11	-.05
16	Brine 6I	8.16	8.16	8.26	8.21	.05

*All derived from the single calibration curve at beginning of run.

interrelated in Figures 16 and 17. The former includes all of the data from runs GB-1 through 4 with the 20 per cent brines and the latter the data from Runs GB-5 and 6 for the 0.2 per cent brines. It is again clear that the data correlate extremely well over the full pH range from 3 to 9. As discussed in connection with Run GB-3, the deviations between the measured and calculated values may well reflect shortcomings in the calculations rather than the sensors.

Reproducibility of Performance - An indication of the reproducibility of the sensor-reference electrode combination is given in Figure 18 in which calibration curves from five different runs are shown. In each case the initial calibration curve was obtained with a fresh reference electrode containing 0.1 m KCl. Three different sensors were involved in these measurements: Y-45 in runs GB-1 and 2, Y-47 in GB-3 and Y-48 in GB-4 and 5. A spread of about 0.5 pH unit is evident for a given output voltage among the initial calibration curves.

If such reproducibility could be maintained it would probably be acceptable for many applications without the need for later recalibration. Unfortunately, significant shifts in the calibration curves occur after prolonged operation because of the exchange of chloride between the reference electrode and the solution being monitored. In monitoring a brine the extent of the shift is limited because of the finite concentration of chloride in the solution. Thus in monitoring a 20 per cent brine (4.278 m NaCl) using a reference containing 0.1 m KCl the theoretical limit on the drift is log (4.278/0.1) or 1.6 pH units. The maximum drift observed during the present tests fell short of this limit by a factor of about two. In monitoring solutions containing no chloride larger drifts are possible through continuous loss of chloride to

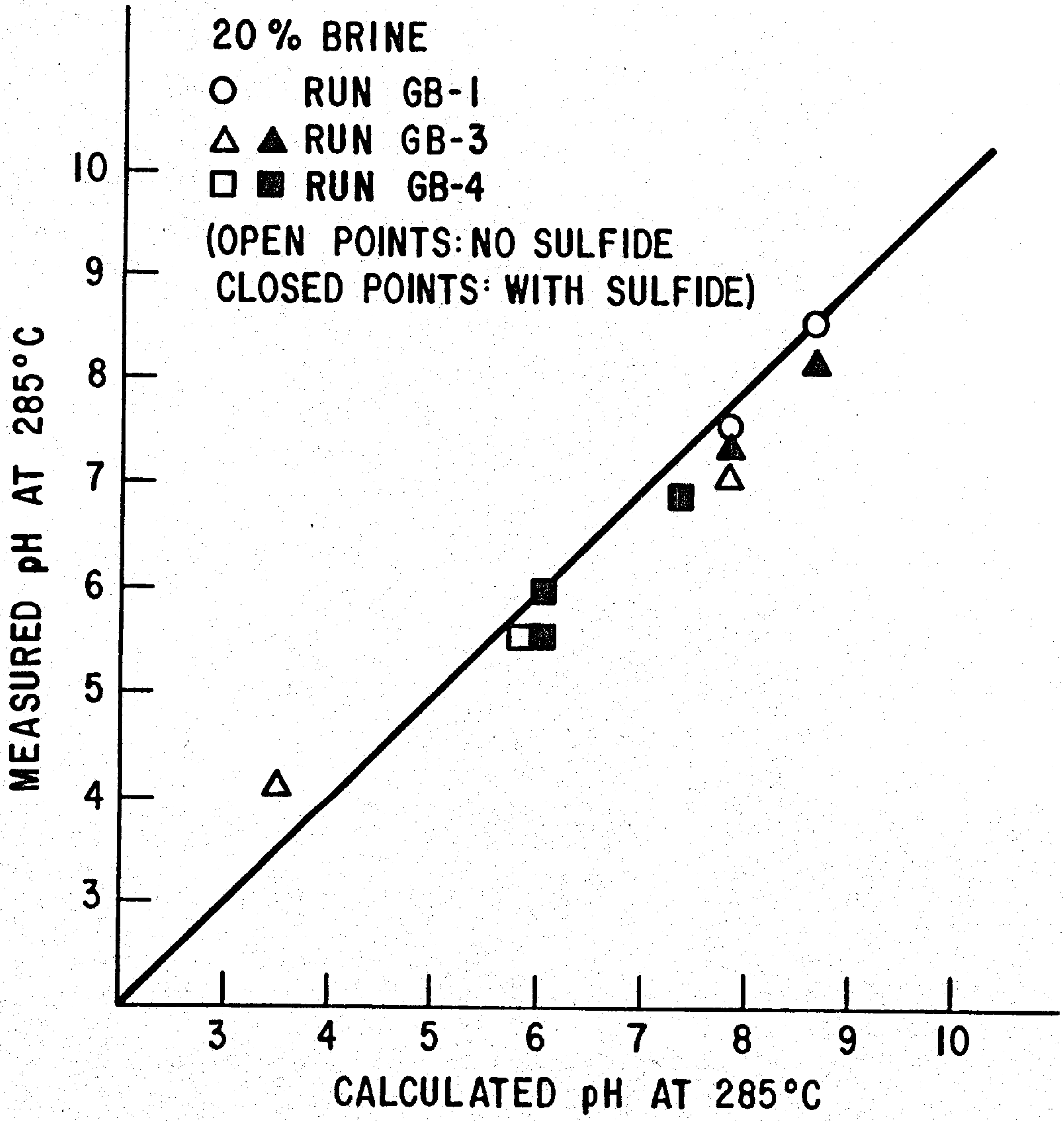

Figure 16. Correlation between measured and calculated pH at 285°C for all 20 per cent brines.

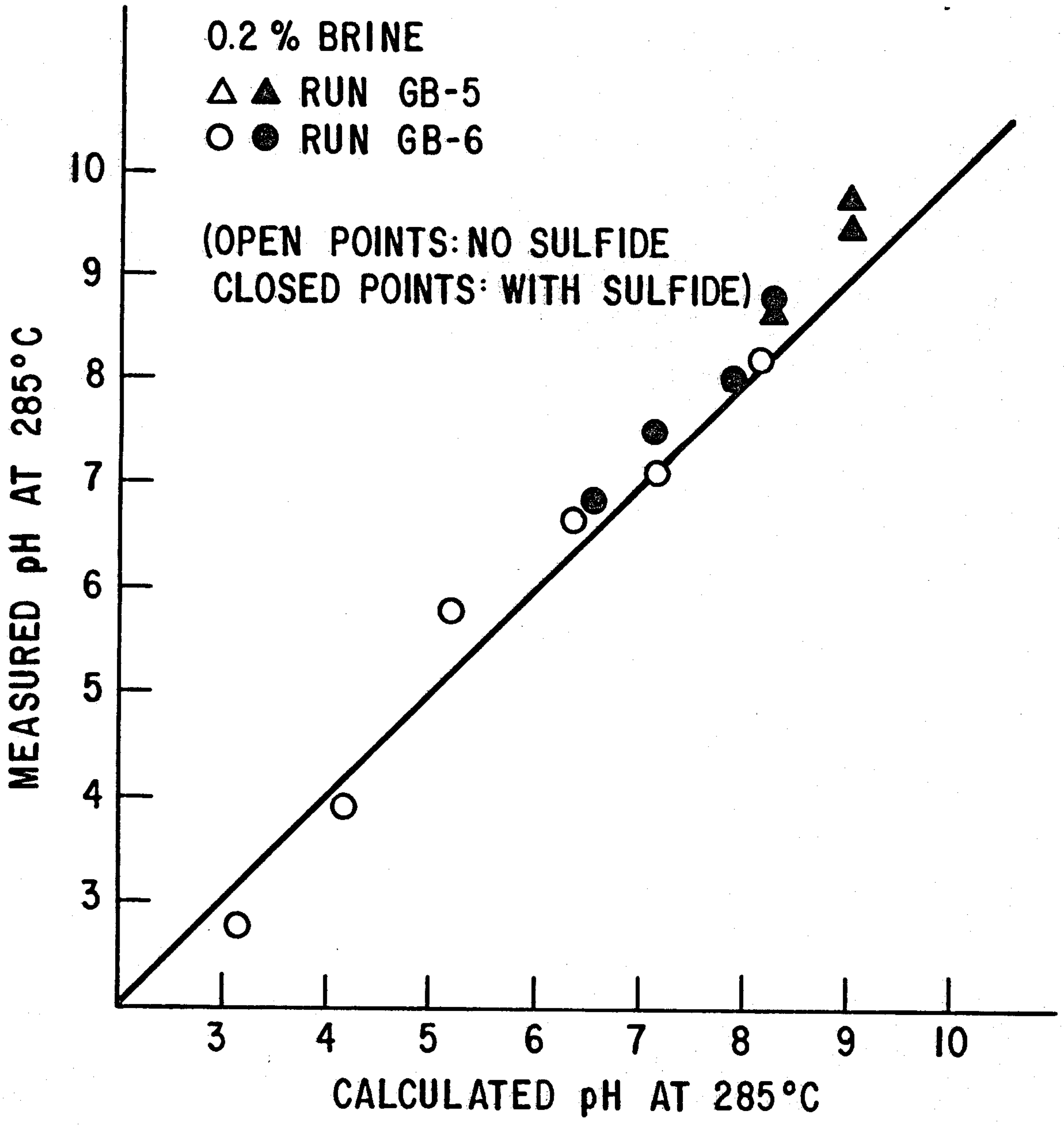

Figure 17. Correlation between measured and calculated pH at 285°C for all 0.2 per cent brines.

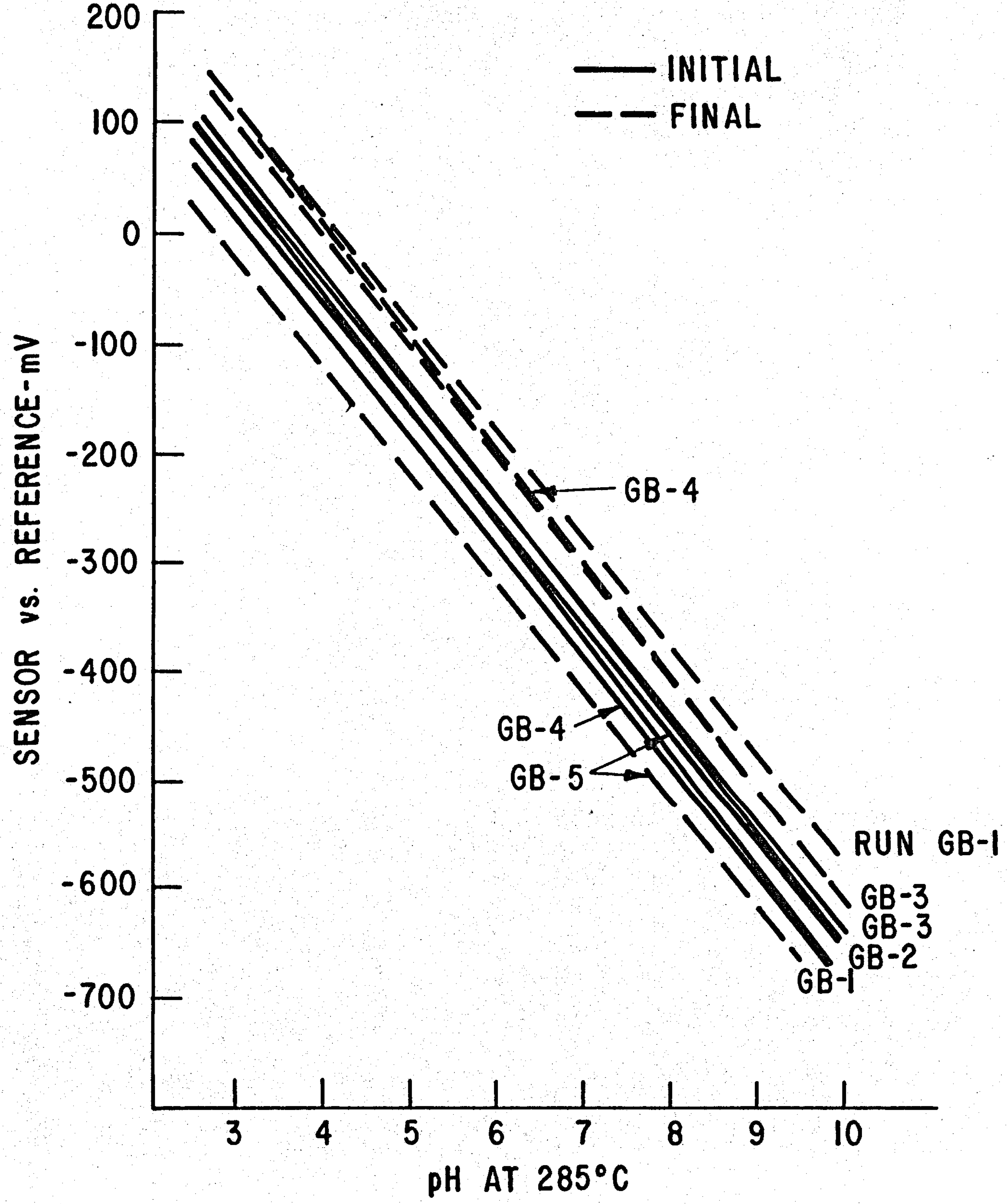

Figure 18. Data showing reproducibility of calibration curves from run to run. All reference electrodes initially contained 0.1 m KCl.

very low concentrations.

While considerable displacement of the calibration curves is encountered, the slope remains quite stable. This suggests that in operation single point calibrations might prove highly satisfactory. In view of the relative stability of the calibration curve obtained against the reference containing 20 per cent sodium chloride in Run GB-3, there would seem the real possibility that a reference electrode might be devised to match a given brine field and thereby give very stable performance in that field. This would be somewhat dependent upon the actual stability of brine levels in the field. Even in such a case occasional recalibration would seem in order.

C. Performance of Sensors at Lower Temperatures (Runs GB-7 and 11/13)

As noted in an earlier report,(2) the standard ceramic has a history of showing a degradation in performance during continuous operation at 95°C. The performance at 95°C has also been poor after brief operation at 285°C even though the same sensor might again perform excellently for weeks at the higher temperature. This behavior has been attributed, at least in part, to structural shortcomings in the ceramic.(2) For this reason low temperature testing was delayed until the end of the present program in order to take advantage of the possible availability of improved materials at that time. This was indeed the case, and four new experimental tubes-all yttria stabilized zirconia-were used in tests at lower temperatures. One of these was a dense ceramic made in house. Used for the fabrication of Sensor SP-8 it was similar to the material used for Sensor SP-4 in Reference 2 which performed well at 95°C for over a month of continuous operation. The other three tubes were obtained from NGK-Locke Insulators, Ltd in Japan. Used in Sensors NGK-A2, NGK-B, and NGK-C1 they were prepared with different process modifications, all of which gave dense ceramic. The tube in NGK-C1 differed from normal in that it incorporated a larger diameter collar on the open end of the tube. This permitted a seal modification that more closely resembled that of a conventional Conax fitting which, it was hoped, would solve some of our seal problems. Unfortunately this hope was not realized in that stress concentration at the junction of the larger diameter collar with the smaller diameter tube resulted in circumferential cracking at that location. Although a disappointment, these initial failures would not seem to be intrinsic to the structure.

None of the new tubes were of the same diameter as those normally employed and slight modifications to the Conax fittings were required. To expedite the tests it was necessary to employ stainless steel fittings for the purpose, and for this reason all of the tests were performed with simple aqueous solutions rather than brines; i.e., water, dilute sulfuric acid and dilute base. This was not felt to be a serious shortcoming in that excellent correlation between the performance of the zirconia sensor on such simple solutions and on brines had by this time been demonstrated in the tests at 285°C.

In Run GB-7 three sensors SP-8, NGK-A2, and NGK-B were tested in parallel at temperatures of 95, 150, 225, and 285°C. Both the pH response and the resistance of each sensor were determined at each temperature. In order to ascertain whether deleterious changes occured at the elevated temperatures a retest at 95°C was performed after each step to a higher temperature. The test results are summarized in Figure 19.

It is evident that Sensor NGK-A2 was erratic from the start and distinct evidence of failure was obtained from the resistance measurement during the

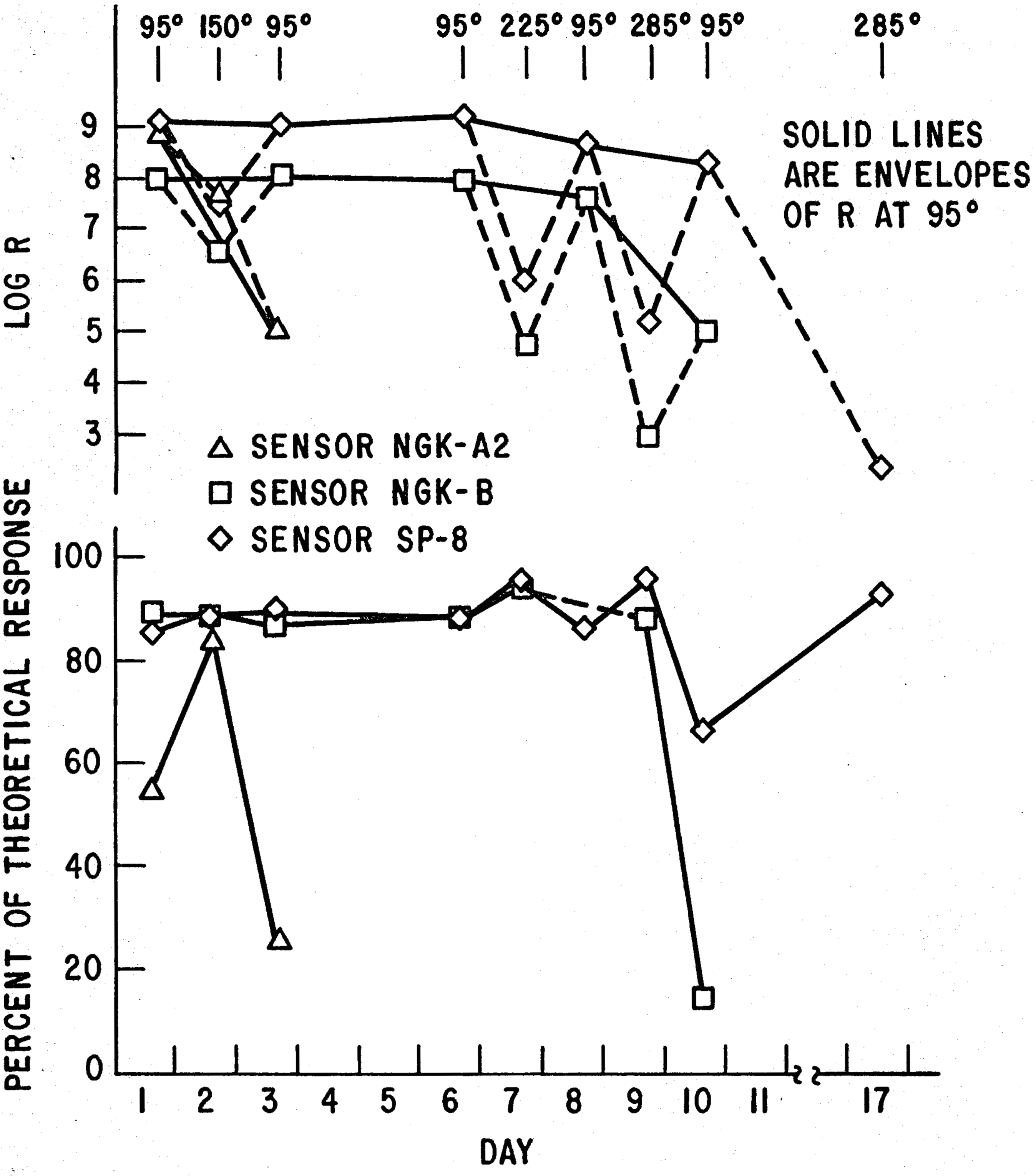

Figure 19. Response and resistance data for several sensors tested alternately at 95°C and higher temperatures.

second test at 95°C. Quite clearly a crack had developed to allow shunting across the ceramic.

The other two sensors performed excellently up through the operation at 285°C although one set of response data for NGK-B at 95°C was lost through an instrument malfunction. Following the exposure at 285°C the subsequent response at 95°C was poorer for both. In the case of NGK-B the low resistance at this point again indicated a shunt across the ceramic, most likely because of a crack. The resistance of SP-8 remained high, however. It is therefore difficult to reach a firm conclusion concerning its decline in performance at 95°C. It could result from degradation of the ceramic, but also from leakage of electrolyte around the seal to form an electrolytic shunt sufficient to degrade performance. We have long suspected such a possiblility in connection with our present seals, but further work will be required to confirm it.

In view of the declining performance at 95°C a final test was performed on SP-8 at 285°C. As anticipated from past experience, the response remained excellent at the higher temperature. At this point the run was terminated and the system cooled to ambient for removal of the sensors. As anticipated both NGK-A2 and NGK-B were found to be cracked. Sensor SP-8 remained solid. However, because a curvature had developed during firing it had been necessary to assemble this sensor <u>in situ</u> while the Conax fitting was mounted in the lid of the autoclave. We were unsuccessful in removing the sensor from the lid without cracking the ceramic tube.

Sensor NGK-C1 was evaluated in a separate test, Run GB-11/13. It was first assembled with a new seal adapted to the collar on the as-received tube. Circumferential cracking occurred during initial operation at 95°C, but the tube could be salvaged and mounted with one of our conventional seals. Performance data are summarized in Figure 20. Upon cooling to 95°C after the test at 225°C the tube again cracked as indicated by the low resistance and poor response. Again the tube was salvagable, and after reassembly it was tested at 95°C and 285°C with satisfactory results. Upon recooling to 95°C the sensor behaved somewhat like SP-8 after its first operating period at 285°C; i.e., poor response but a high resistance. At this point the run was discontinued. Close examination of the sensor revealed an obscure crack which may have been responsible for the final behavior at 95°C.

Although the present series of tests were not completely satisfying, they do indicate that ceramics can be made that are more stable in low temperature service than the standard Corning ceramic used in the bulk of the tests and most of the earlier work. It is, however, not yet clear whether the degradation in performance of the new ceramics at low temperatures is a reflection of changes in the ceramic or defects in the seals. While we strongly suspect the latter, this point requires resolution. In the interim it appears likely that it will be possible to operate sensors employing one of the new ceramics for extended times at low temperature (i.e., 95-150°C) if excursions to higher temperatures are avoided.

D. Operation at 5000 psi

The ability of the new pH sensor to operate at 5000 psi and 285°C was demonstrated in a single experiment. It was originally planned to conduct this test in a Ticode-12 autoclave using an air operated hydraulic pump (SC Hydraulic Engineering Corp., Los Angeles, CA. Model 1-600-10) for pressurization. The system had been used on an earlier DOE contract and was made avail-

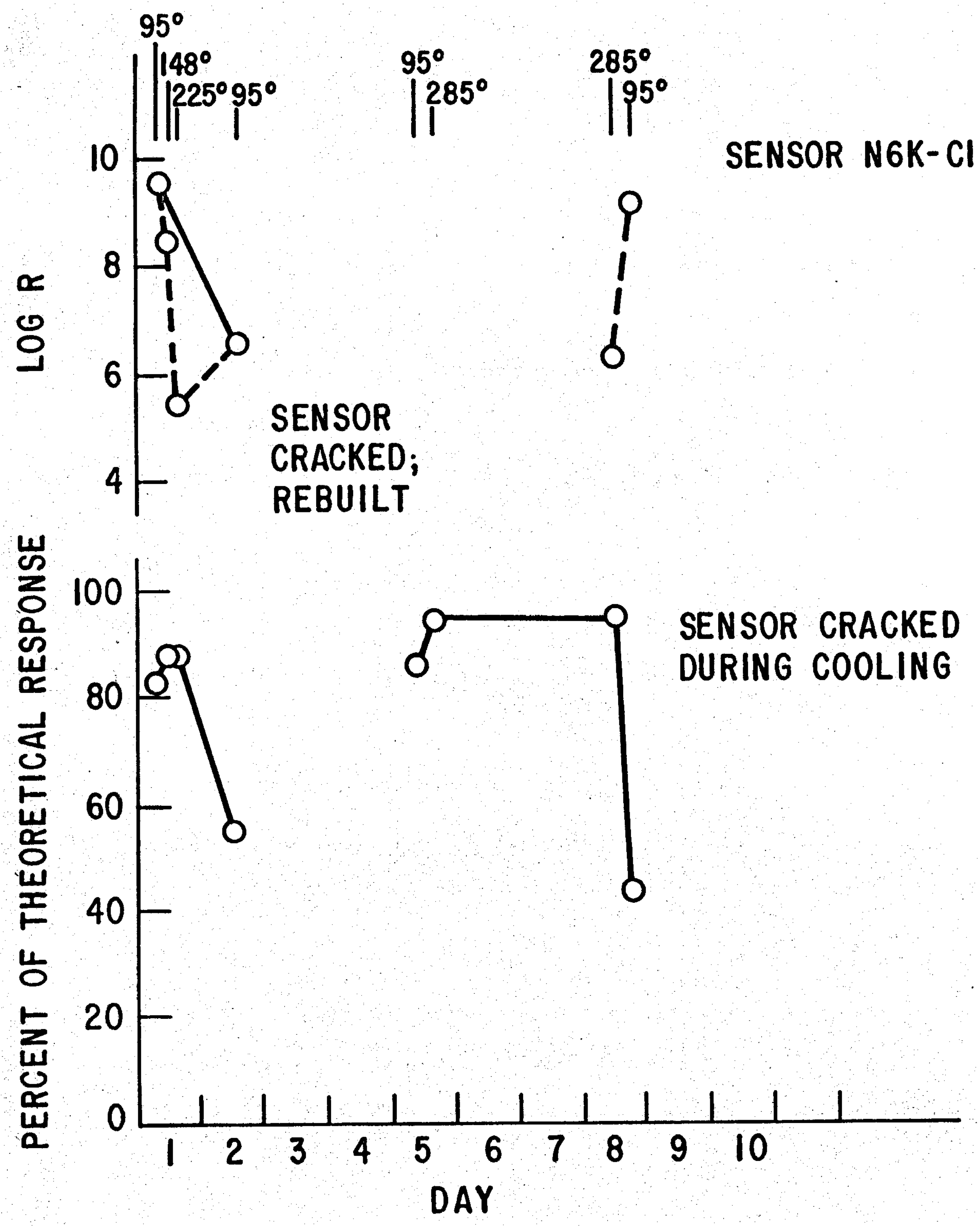

Figure 20. Response and resistance data for sensor NGK-Cl tested alternately at 95°C and higher temperatures.

able to us. Because the test was conducted in a concrete cell in another building as a safety precaution, complexity was kept to a minimum. It was planned to bring the system to pressure with water, shift to a neutral brine and then introduce pH transients to demonstrate response.

Unfortunately the closure on the new autoclave employed a Kalrez ''O''-ring that was not designed for operation at 285°C, and in an initial trial the gasket failed during heat-up. We therefore substituted one of our standard 316 stainless steel autoclaves (Autoclave Engineers, Inc., Erie, Pa.) while utilizing the pump from the loaned equipment. This arrangement functioned satisfactorily but limited our exposure to water, dilute sulfuric acid and dilute sodium hydroxide. Data obtained from the short run are summarized in Table XX. They demonstrate the ability of the sensor to withstand the 5000 psi pressure at 285°C and to respond to a pH transient under these conditions. Upon completion of the test the pH sensor remained intact.

E. Demonstration of Calibration System

From the inception of the program the need for a simple calibration system for the sensor-reference electrode combination has been stressed. For the most precise measurements calibration should be done with at least two standards. For less precision, one will do.

In either case a straightforward method of introducing the sample stream and the standards to the sensor is required. To illustrate a possible approach, the unit shown diagramatically in Figure 21 was assembled. Central to the system was a small volume autoclave (~70 ml, but a smaller volume would be feasible, and preferable) for the sensor-reference combination to reduce the time required to reach steady state. This unit could be valved to a brine

Table XX

SUMMARY OF OPERATING CONDITIONS AND DATA FROM HIGH PRESSURE RUN GB-10

P = 5000 psi; T = 285°C

Lapsed Time-hr	Temp °C	Pressure psi	Solution in Autoclave		Measured Potentials, mV Glass Electrode at 25°C	 Sensor at 285°C	 Pt Electrode at 285°C	Notes
0	25	Ambient	Water					Start pressurization
0.1	25	1250	"					Start heating
1.8	288	1250	"		-10	-475	-75	Increase pressure
2.0	285	5000	"					
2.1	285	4900	"		50	-492	-8	
2.2								Inject 4.0 cc 0.1 $\underline{m}H_2SO_4$
2.6	285	5150	~0.0005 $\underline{m}H_2SO_4$		216	-68	394	
3.4	285	5150	"		202	-81	400	
3.7	285	5150	"		199	-86	400	
	285	5150	"	mean	206	-78	398	
3.7								Inject 8.0 cc 0.2 $\underline{m}$ NaOH
4.0	285	5150	~0.001 $\underline{m}$ NaOH		-225	-508	-78	
4.1	285	5150	"		-225	-511	-82	
4.4	284	5100	"		-220	-510	-74	
4.8	285	5100	"		-217	-506	-66	
7.0	285	5100	"		-216	-480	-22	
			"	mean	-221	-503	-64	
		Δ mV (acid to base)			427	425	462	
		Theoretical			473	543	543	
		Percent of Theory			90	78	85	

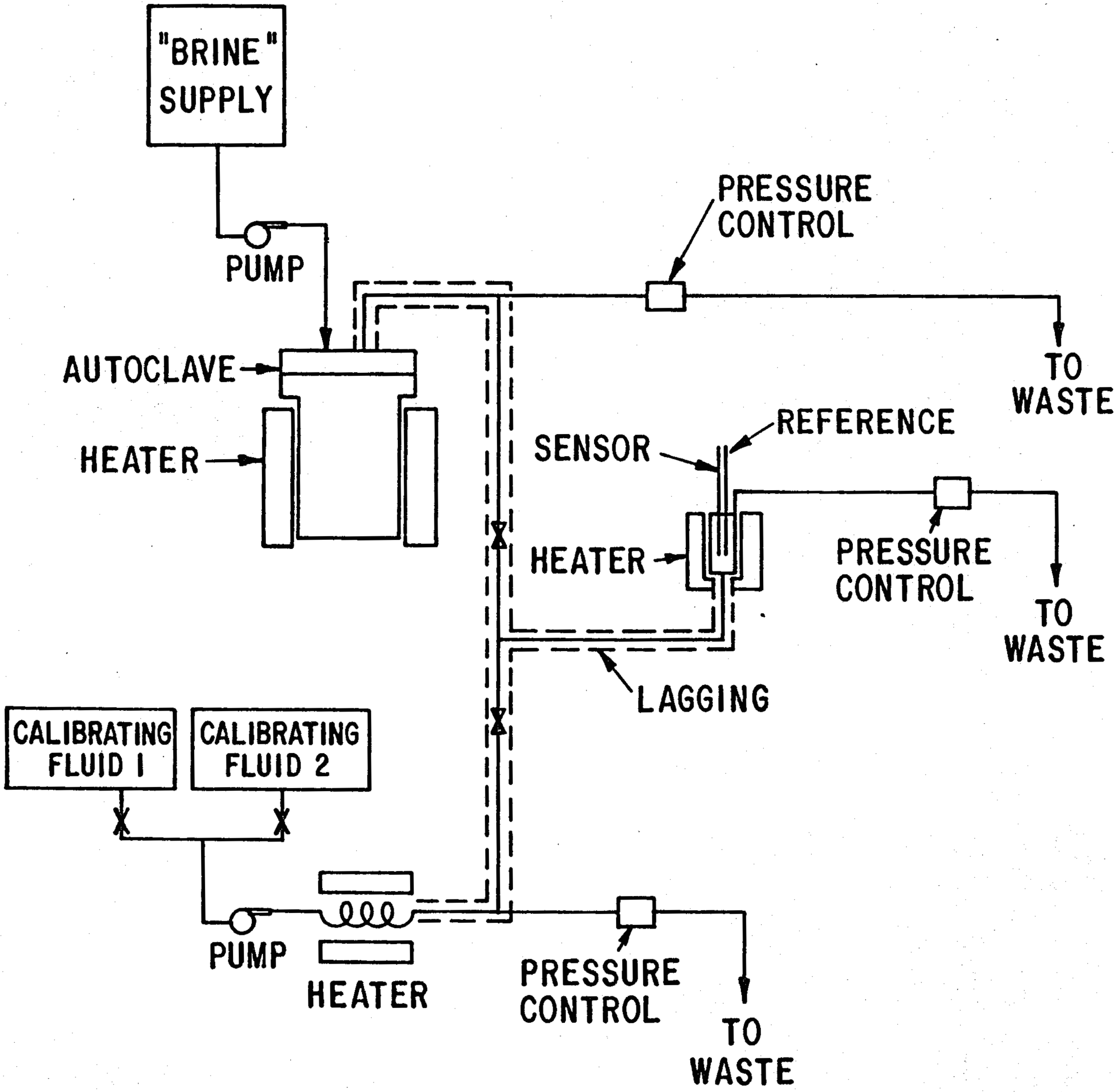

Figure 21. Schematic diagram of the sampling/calibration system.

line being monitored or to a supply of calibration standards. For demonstration purposes the brine line was simulated by an autoclave that provided a hot sample stream to the monitoring unit. In order to preheat the cold standard solutions before they reached the monitor a separate heating coil was used with its own individually controlled heater. A ten foot long coil of 1/8 inch o.d. tubing was used for this purpose. It was mounted in a tube furnace with a Love temperature controller.

The system was run only briefly for demonstration purposes, and pure water was used as a stand-in for the brine. The individual controllers on the ''brine supply,'' the monitoring unit, and the pre-heater for the standard solutions were set to maintain each unit at about 285°C. Once steady operation was achieved 0.0005 $\underline{m}$ H_2SO_4 and 0.001 $\underline{m}$ NaOH were used to obtain an initial calibration curve. Because of the volume of the monitoring unit and the transfer lines about 30-60 minutes were required to reach steady state with each stream when a flow-rate of about 12 ml/minute was employed. Operation was then transferred to the water. When a steady potential was reached it was recorded and the pH was read from the calibration curve. Over the two days of operation two calibration curves and three sets of readings on the water were made. Operating conditions and data are summarized in Table XXI, and the calibration curves are in Figure 22. As evident from Figure 22 some drift in the calibration curve occurred even in this short period, but by reading the pH from the appropriate curve the value for the incoming stream was found to remain close to the theoretical value for water at 285°C. Had all the pH values for the water been estimated from the original calibration curve larger deviations from the theoretical would have been obtained, cf. Table XXII. While the drift over a period of two days is not significant, the data do il-

Table XXI

SUMMARY OF OPERATING CONDITIONS AND DATA

FROM CALIBRATING SYSTEM - RUN GB-12

T = 285°C

Lapsed Time-hr	Operation	Potential of Sensor Y-53 vs Reference RD-19, mV
0	Start operation on water from autoclave	
24	Continuing operation on water from autoclave	-270
	To calibration solution - 0.0005 mH_2SO_4	
26	On 0.0005 mH_2SO_4	-42
	To second calibration solution - 0.001 m NaOH	
26.8	On 0.001 m NaOH	-545
	Return to water from autoclave	
42.3	On water	-242
	To 0.0005 mH_2SO_4	
44.2	On 0.0005 mH_2SO_4	-20
	To 0.001 m NaOH	
46.8	On 0.001 m NaOH	-510
	Return to water from autoclave	
49.3	On water	-247
	Test terminated because of leaking valve	

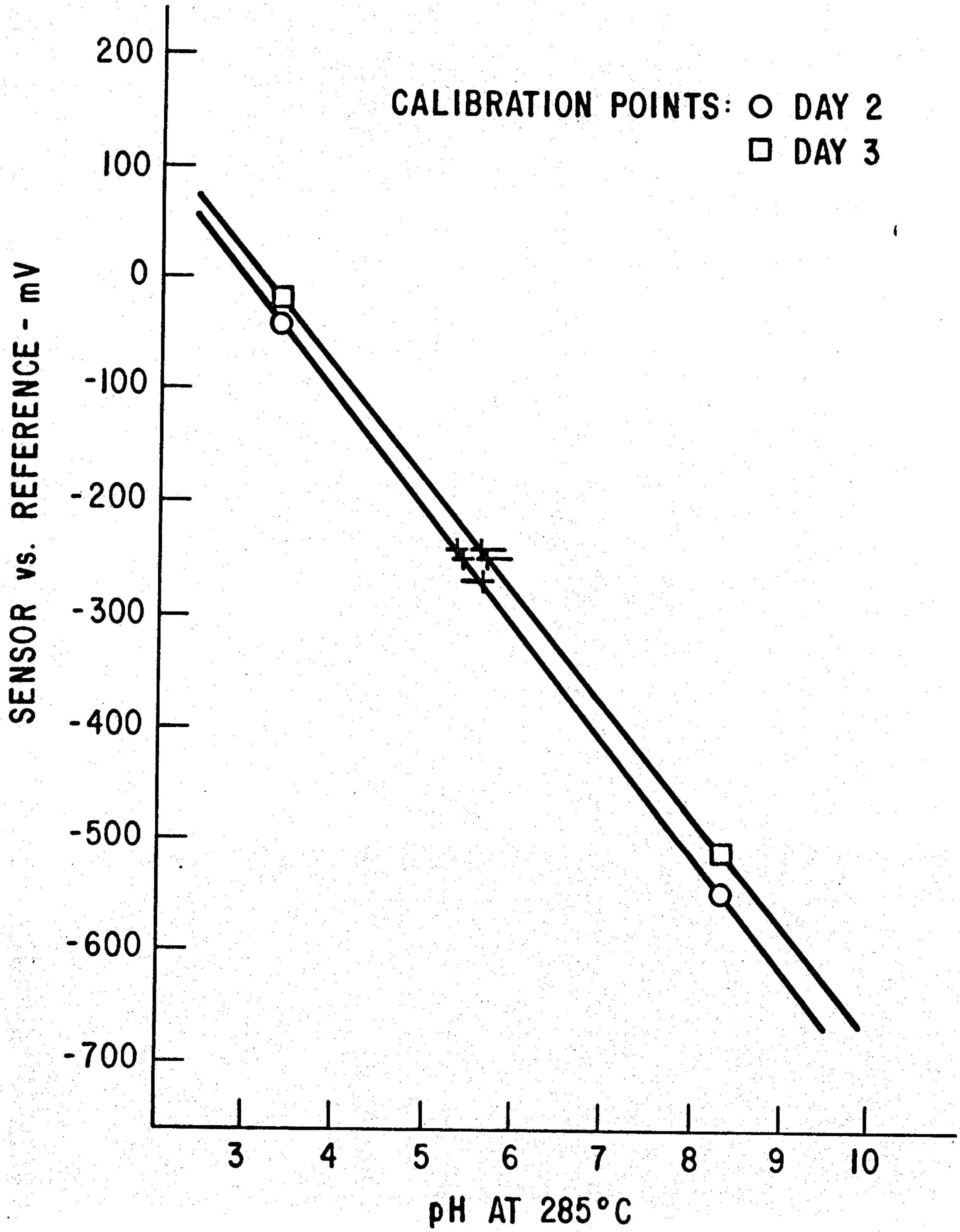

Figure 22. Calibration curves obtained with the new sampling/calibration system.

Table XXII

COMPARISON OF MEASURED AND CALCULATED VALUES OF pH IN RUN GB-12 WITH CALIBRATION UNIT

	Calculated pH	Measured pH		Δ pH Meas.-Calc.	
Day 2	5.68	5.58		-0.10	
Day 3	5.68	5.58	(5.30)	-0.10	(-0.38)
Day 3	5.68	5.62	(5.35)	-0.06	(-0.33)

Note: Values in parenthesis were obtained using calibration curve from Day 2 lustrate the type of behavior that would be expected to be encountered over the long term. During the operating period the temperature in the monitoring unit could be maintained at 285±1°C.

Although this limited demonstration does not establish the design of a prototype system, it does demonstrate the general feasibility of the approach. In further refinements a smaller chamber would be employed for the sensor-reference combination in order to facilitate more rapid turnover. Better valves would also be substituted for control purposes, and it is hoped that one of the heating units can be eliminated.

V. REFERENCES

1. L.W. Niedrach, J. Electrochem. Soc. 127, 2122 (1980).

2. L.W. Niedrach and W.H. Stoddard, ''The Development of a High Temperature pH Electrode for Geothermal Fluids. Final Report-Task I'' prepared for the Pacific Northwest Laboratory operated by Battelle Memorial Institute under prime contract No. DE-AC-06-76-RLO-1830 for the United States Department of Energy, Division of Geothermal Energy, Report No. PNL 3857 UC-66, March 1981.

3. M.J. Danielson, Corrosion 35, 201 (1979).

4. B.C. Syrett, D.D. Macdonald, H. Shih, and S.S. Wing, Corrosion Chemistry of Geothermal Brines. Part 2: High Salinity Brine, Final Report (Part 2) to NSF (RANN) and DOE, Washington, D.C. NSF (RANN) Grant No. AER 76-00713 (1977).

5. ''Methods Manual for Hach Direct-Reading Engineer's Laboratory Model DR-EL/4,'' Hach Chemical Company, 1980. Cf. APHA Standard Methods, 14th. Ed., p. 503 (1975).

6. R.A. Robinson and R.H. Stokes, ''Electrolyte Solutions,'' Second Edition (Revised), Butterworths, London, 1970.

7. H.S. Harned and R.A. Robinson, ''Multicomponent Electrolyte Solutions,'' Pergamon Press, London, 1968.

Appendix A

PROCEDURES USED FOR pH CALCULATIONS

In order to estimate the pH values for the brine solutions we have adapted a computer program developed by Syrett, et al[(1A)]. As originally written the program was directed towards saline solutions containing varying amounts of carbonic acid and hydrogen sulfide including their dissociation products. Although provision was made to accommodate the two dissociation steps of the carbonic acid and the hydrogen sulfide, provision was not made for the presence of salts of the above acids.

We have broadened the program to allow for the presence of such salts by including a term in the overall equation for mass and charge balance for the equivalent base required to form such salts from the acids; i.e., the last term in the following equation:

$$\begin{aligned} a_{H+}^{3} &- a_{H+} [K_3 \, (H_2S) \, \gamma_0 + K_1 (H_2CO_3) \, \gamma_0 + K_W] \\ &- 2(\mathrm{gamma}_1/\gamma_2) \, [K_1K_2 \, (H_2CO_3) \, \gamma_0 + K_3K_4 \, (H_2S) \, \gamma_1] \\ &+ a_{H+}^{2} \, \gamma_1 \sum_{0}^{m} m \, M^{m+} = 0 \end{aligned} \qquad (1)$$

We have also added terms for the activity coefficients of the undissociated acids since these deviate significantly from 1.0 in concentrated brines as evidenced by solubility data in the presence of salts[(2A,3A)].

In order to relate directly to our experimental protocols an additional variation was introduced into the program to permit the derivation of the ambient temperature (25°C) composition on the basis of the NaCl content and the equivalent base concentration (from the amounts of sodium bicarbonate, sodium carbonate and sodium sulfide added) of the starting solution and the percent carbon dioxide in the equilibrating gas. Following this the composition at a second temperature of interest - 285°C in our experiments - is made from the 25°C values.

The dissociation constants and most of the additional thermodynamic data required for the calculations were those used by Syrett, et al. which they, in turn, had adopted from Naumov et al(4A). In addition we employed data from Seidell(2A) to derive the solubility coefficient for carbon dioxide at 25°C in terms of the partial pressure as well as γ_0 at 25°C. In turn, γ_0 at 285°C was estimated from the data of Ellis and Golding(3A) for the solubility of carbon dioxide in water and sodium chloride solutions above 100°C. For extrapolation to 4.278 $\underline{m}$ their data, which extended only to 2.0 $\underline{m}$ NaCl, was fitted by least squares to the Setchenow equation

$$\log \gamma_0 = \log(K/K^\circ) = BC \qquad (2)$$

where K° is the solubility coefficient in water, K is the coefficient in brine at concentration C, and B is a constant. For the more dilute brines having an ionic strength of about 0.1 $\underline{m}$ or less, γ_0 was assumed equal to 1.0.

To obtain the pH for any given set of conditions equation 1 in combination with the various dissociation equilibria for the two acids is solved using the Newton-Raphson iterative technique. This in turn permits the calculation of the concentrations of all other relevant species. Using this program the ambient temperature and 285°C pH values and concentration profiles for all of the carbonate solutions used in this work were calculated; the results are summarized in Appendix B. Also included in the tables are related data for the simple brine solutions containing HCl and NaOH. The program itself is listed on the following pages.

References

1A. B.C. Syrett, D.D. Macdonald, H. Shih, and S.S. Wing, Corrosion Chemistry of Geothermal Brines. Part 2: High Salinity Brine, Final Report (Part 2) to NSF (RANN) and DOE, Washington, D.C. NSF (RANN) Grant No. AER 76-00713 (1977).

2A. A. Seidell and W.F. Linke, ''Solubilities of Inorganic and Metal-Organic Compounds,'' Vol. I, London, D. Van Nostrand Co., Inc., 1958 pp. 467 ff.

3A. A.J. Ellis and R.M. Golding, Am. J. Sci. 261, 47 (1963).

4A. G.B. Naumov, B.N. Ryzhenko, and I.L. Khodakovsky, Handbook of Thermodynamic Data, Transl. U.S. Geological Survey, USGS-WRD-74-001 (1974).

```
10c      this program calculates the ph of brine solutions.
20c      it is based upon an earlier program of syrett, macdonald,
30c      et al. (nsf(rann) grant no.aer 76-00713; final report
40c      december 16, 1977)
50c
60c
90       real nac, is, oh, ks
100c
110      call fparam(1,80)
112  107 format (///,50x
113 &    "brine20",
114 &    "  (rev. of ",
115 &    "1/14/82",
116 &    ")")
118c
120c     input------------
130      temp2 = 285.
140      pcco2 = 1.
150      ts = 100.
160      cnacl = 0.0342
170      nac = 0.00688
172      gamma01 = 1.
174      gamma02 = 1.
180c     --------------------
190c
200      real ch2co3,ch2s,x,y, k1,k2,k3,k4,kw,pk1,pk2,pk3,pk4,pkw
205      t = 25.
210      TEMP = T
220      t = t + 273.15
230      tsi = ts
240      if(t.eq.0.)go to 14
250      ts=(ts/34.)*0.001
270      pk1 = (2022.5/t)-5.982+0.018686*t
280      pk2 = (2523.7/t)-4.096 + 0.020026*t
290      pk3 = (3539.1/t) - 12.41 + 0.025220*t
300      pk4 = (4668.0/t)-9.53 +0.022760*t
310      ks = 4.45 e-5
320      k1 = 10.**(-pk1)
330      k2 = 10.**(-pk2)
340      k3 = 10.**(-pk3)
350      k4 = 10.**(-pk4)
360      pkw = (4466.2/t)-5.941+0.016638*t
370      kw = 10.**(-pkw)
380      e = (5321./t) + 233.76 - .9297*t+.001417*t*t-.0000008292*t*t*t
390      a = 1.8246e+06/((e*t)**1.5)
400      b = 50.294e+08/((e*t)**0.5)
410      is = cnacl
420      ph = 4.0
430      aho = 10.**(-ph)
440   20 continue
450      gamma0 = gamma01
460      gamma1 = a*(is**.5)/(1. + (4.5e-08)*b*(is**.5))
470      gamma2 = 4.*a*(is**.5)/(1. + (7.5e-08)*b*(is**.5))
480      gamma1 = 10.**(-gamma1)
490      gamma2 = 10.**(-gamma2)
```

```
500        ic = 0
510        do 200 k = 1,100
520        ic = ic + 1
530        ph = -alog10(aho)
540        z = gamma1*gamma2*aho**2 + gamma0*gamma2*k3*aho
542 &      + gamma0*gamma1*k3*k4
550        w = gamma1*gamma2*aho**2 + gamma0*gamma2*k1*aho
552 &      + gamma0*gamma1*k1*k2
560        ch2co3 = ks*760.*pcco2/(100.*gamma0)
570        ch2s = ts*gamma1*gamma2*aho**2/(z)
580        x1 = k1*ch2co3*gamma0
590        x2 = k3*ch2s*gamma0
600        x3 = kw
610        x = x1 + x2 + x3
620        y = 2.*k1*k2*ch2co3 + 2.*k3*k4*ch2s
630        y = y*gamma0
640        chco3 = ch2co3*gamma0*k1/(gamma1*aho)
650        cco3 = ch2co3*gamma0*k1*k2/(gamma2*aho**2)
660        f1 = aho**3
670        f2 = x*aho
680        f3 = y*(gamma1/gamma2)
690        f4 = gamma1*nac*aho**2
700        f = f1 - f2 - f3 + f4
720        zz = 1./(gamma1*aho**2)
730        ff1 = f1*zz
740        ff2 = f2*zz
750        ff3 = f3*zz/2.
760        ff4 = f4*zz
770        df = 3.*aho**2 - x + gamma1*nac*aho*2.
780        ah=aho-f/df
790        tah = (ah-aho)/aho
800        taha = abs(tah)
810        IF(TAHA - 0.0001) 2,2,1
820      1 continue
830        aho=ah
840    200 continue
850      2 continue
870        ph = -alog10(ah)
880        if(ic.eq.100)print 104
890        ab=gamma1*gamma2*ah*ah*ah
900        ac =gamma2*k3*ah*ah
905        ac = ac*gamma0
910        ad = gamma1*k3*k4*ah
915        ad = ad*gamma0
920        ae = gamma2*k1*ah*ah
925        ae = ae*gamma0
930        af=gamma1*k1*k2*ah
935        af = af*gamma0
940        cc = ch2co3
950        cs = (ts*ab)/(ab + ac + ad)
970        chsm=k3*cs/(gamma1*ah)
980        chsm = chsm*gamma0
990        cs2m = k4*chsm/(gamma2*ah)
1000        cs2m = cs2m*gamma1
1010        chco3M = k1*cc/(gamma1*ah)
```

```
1020          chco3m = chco3m*gamma0
1030          cco32m = k2*chco3m*gamma1/(gamma2*ah)
1040          cohm = kw/(ah*gamma1)
1070          is = cnacl + (chsm + chco3m + cohm + 4.*(cco32m + cs2m) + nac)/2.
1080          tah1=abs((chco3m-chc)/chco3m)
1090          tah2=abs((cs-ch2s)/cs)
1100          if(ic - 3) 16,16,3
1105       16 continue
1110          if(tah1 - 0.001) 4,4,3
1120        3 continue
1130          ch2co3=cc
1140          chc=chco3m
1150          ch2s=cs
1160          go to 20
1170        4 continue
1180          ch=ah/gamma1
1190          sh = -alog10(ah)
1200          ohm = kw/(ah*gamma1)
1210          tc = (ch2co3 + chco3m + cco32m)*44.
1220          tc = tc*1000.
1230          tci = tc
1235          print 107
1240          print 101
1250          print 103
1260          print 102, temp, pcco2, tci, tsi, cnacl, nac, gamma01, gamma02
1270          print 100
1280          print 103
1290          print 106, temp,sh,cc,chco3m,cco32m,cs,cnsm,cs2m,ohm,
1300 &        gamma1, gamma2
1310C
1320C
1330C      ------------------------------------------------------------------------
1340C
1350C
1360          temp = temp2
1370          t = temp + 273.15
1470          tc = tci
1480          ts = tsi
1490          ts=(ts/34.)*0.001
1500          tc =(tc/44.)*0.001
1510          pk1 = (2022.5/t)-5.982+0.018686*t
1520          pk2 = (2523.7/t)-4.096 + 0.020026*t
1530          pk3 = (3539.1/t) - 12.41 + 0.025220*t
1540          pk4 = (4668.0/t)-9.53 +0.022760*t
1550          k1 = 10.**(-pk1)
1560          k2 = 10.**(-pk2)
1570          k3 = 10.**(-pk3)
1580          k4 = 10.**(-pk4)
1590          pkw = (4466.2/t)-5.941+0.016638*t
1600          kw = 10.**(-pkw)
1610          e = (5321./t) + 233.76 - .9297*t+.001417*t*t-.0000008292*t*t*t
1620          a = 1.8246e+06/((e*t)**1.5)
1630          b = 50.294e+03/((e*t)**0.5)
1640          is = cnacl
1650          ph = 4.0
```

```
      aho = 10.**(-ph)
    9 continue
      gamma0 = gamma02
      gamma1 = a*(is**.5)/(1. + (4.5e-08)*b*(is**.5))
      gamma2 = 4.*a*(is**.5)/(1. + (7.5e-08)*b*(is**.5))
      gamma1 = 10.**(-gamma1)
      gamma2 = 10.**(-gamma2)
      ie = 0
      do 202 m = 1,100
      ie = ie + 1
      ph = -alog10(aho)
      z = gamma1*gamma2*aho**2 + gamma0*gamma2*k3*aho
 &    + gamma0*gamma1*k3*k4
      w = gamma1*gamma2*aho**2 + gamma0*gamma2*k1*aho
 &    + gamma0*gamma1*k1*k2
      ch2co3 = tc*gamma1*gamma2*aho**2/(w)
      ch2s = ts*gamma1*gamma2*aho**2/(z)
      x1 = k1*ch2co3*gamma0
      x2 = k3*ch2s*gamma0
      x3 = kw
      x = x1 + x2 + x3
      y = 2.*k1*k2*ch2co3 + 2.*k3*k4*ch2s
      y = y*gamma0
      chco3 =tc*gamma2*k1*aho/w
      cco3 = tc*gamma1*k1*k2/w
      f1 = aho**3
      f2 = x*aho
      f3 = y*(gamma1/gamma2)
      f4 = gamma1*nac*aho**2
      f = f1 - f2 - f3 + f4
      zz = 1./(gamma1*aho**2)
      ff1 = f1*zz
      ff2 = f2*zz
      ff3 = f3*zz/2.
      ff4 = f4*zz
      df = 3.*aho**2 - x + gamma1*nac*aho*2.
      ah=aho-f/df
      tah = (ah-aho)/aho
      taha = abs(tah)
      if(taha - 0.0001) 11,11,10
   10 continue
      aho=ah
  202 continue
   11 continue
      ph = -alog10(ah)
      ab=gamma1*gamma2*ah*ah*ah
      ac =gamma2*k3*ah*ah
      ac = ac*gamma0
      ad = gamma1*k3*k4*ah
      ad = ad*gamma0
      ae = gamma2*k1*ah*ah
      ae = ae*gamma0
      af=gamma1*k1*k2*ah
      af = af*gamma0
      cc=(tc*ab)/(ab+ae+af)
```

```
2180        cs = (ts*ab)/(ab + ac + ad)
2200        chsm=k3*cs/(gamma1*ah)
2210        chsm = chsm*gamma0
2220        cs2m = k4*chsm/(gamma2*ah)
2230        cs2m = cs2m*gamma1
2240        chco3m = k1*cc/(gamma1*ah)
2250        chco3m = chco3m*gamma0
2260        cco32m = k2*chco3m*gamma1/(gamma2*ah)
2270        tah1=abs((cc-ch2co3)/cc)
2280        tah2=abs((cs-ch2s)/cs)
2290        is = cnacl + (chsm + chco3m + cohm + 4.*(cco32m + cs2m) + nac)/2.
2292        if(ie -3) 15,15,12
2294     15 continue
2300        if(tah1 - 0.001) 13,13,12
2310     12 continue
2320        ch2co3=cc
2330        ch2s=cs
2340        go to 9
2350     13 continue
2360        ch=ah/gamma1
2370        sh = -alog10(ah)
2380        ohm = kw/(ah*gamma1)
2390        print 106, temp,sh, cc,chco3m,cco32m,cs,chsm,cs2m,ohm,
2400 &      gamma1,gamma2
2420     14 continue
2430    100 format (///,1x, "temp", 2x, "ph",
2440 &      4x, "ch2co3",
2450 &      2x, "chco3",
2460 &      3x, "cco3",
2470 &      4x, "ch2s",
2480 &      5x, "chs",
2490 &      5x, "cs",
2500 &      6x, "coh",
2510 &      4x, "gam1",
2520 &      2x, "gam2")
2530    101 format(/, 1x, "temp",
2540 &      4x, "pcco2",
2550 &      4x, "tc(ppm)",
2560 &      4x, "ts(ppm)",
2570 &      4x, "cnacl(m)",
2580 &      4x, "nac(m)",
2582 &      4x, "gam01",
2584 &      4x, "gam02")
2590    102 format(f5.0,
2600 &      f8.0,
2610 &      F11.0,
2620 &      f10.0,
2630 &      f12.3,
2640 &      1pe13.2,
2642 &      0pf8.3,
2644 &      f9.3)
2650    103 format (" ")
2660    104 format(2x,"no convergence")
2670    105 format(////)
2680    106 format(f5.0,f5.2,
```

```
2690 &      10e9.1, 2e8.1,
2700 &      4e3.1,
2710 &      0pf7.3, f6.3)
2720        stop
2730        end
```

Appendix B

SUMMARY OF DETAILED COMPOSITION DATA FOR THE BRINES USED IN TESTS

(As Calculated Using Program of Appendix A)

Table IA is identical with Table VI in the body of the report and will aid in linking the more detailed compilations to the individual tests.

In each of the subsequent tables the input conditions are first listed. These are followed by the equilibrium conditions at 25 and 285°C. For the calculations for the simpler brines containing only HCl or NaOH in addition to the saline, a simplification of the program in Appendix A was employed. This placed major emphasis on the calculation of the appropriate activity coefficients.

In connection with the tabulations the following definitions pertain to the column headings:

PCCO2 = Percent CO_2 in equilibration gas.

TC = Total carbonate in solution after equilibration with the gas; as ppm CO_2.

TS = Total sulfide present as ppm H_2S.

CNACL = Concentration of NaCl in terms of moles/1000g H_2O.

NAC = Equivalent base = $[NaHCO_3] + 2\ [Na_2CO_3] + 2\ [Na_2S]$ as moles/1000g H_2O.

GAMO1 = Activity coefficient for H_2CO_3 at 25°C as derived from data in Seidell; cf. Appendix A.

GAMO2 = Activity coefficient for H_2CO_3 at $285^\circ C$ from data of Ellis and Golding; cf. Appendix A.

CH2CO3 = Concentration of H_2CO_3; moles/1000g H_2O.

CHCO3 = Concentration of HCO_3; moles/1000g H_2O.

CCO3 = Concentration of CO_3^{-2}; moles/1000g H_2O.

CH2S = Concentration of H_2S; moles/1000g H_2O.

CHS = Concentration of HS^-; moles/1000g H_2O.

CS = Concentration of S^{-2}; moles/1000g H_2O.

COH = Concentration of OH^-; moles/1000g H_2O.

GAM1 = Activity coefficient of monovalent ions.

GAM2 = Activity coefficient of divalent ions.

Table IA

COMPOSITIONS OF FEED SOLUTIONS USED IN RUNS GB-1 THROUGH 6

Run No.	Brine No.	[NaCl] m	Equivalent Base** m	$[H_2S]$ ppm	Percent CO_2 in equilibrating gas	Calculated pH 25°C	Calculated pH 285°C
GB-1	1A*	4.278 (20%)	0.109	-	1.0	8.6	8.6
	1B	4.278	0.109	-	100.0	6.6	7.8
GB-2	2A*	4.278	0.00109	-	100.0	4.6	5.8
GB-3	3A	4.278	(containing 0.001m HCl)		N_2	3.3	3.5
	3B	4.278	(containing 0.001m NaOH)		N_2	10.7	7.8
	3C(=1A)	4.278	0.109	-	1.0	8.6	8.6
	3Cs*	4.278	0.110	10	1.0	8.6	8.6
	3Ds	4.278	0.110	10	100.0	6.6	7.8
GB-4	4A(=2A)	4.278	0.00109	-	100.0	4.6	5.8
	4As*	4.278	0.00168	10	100.0	4.8	6.0
	4Bs	4.278	0.00168	10	1.0	6.8	7.3
GB-5	5As*	0.0342 (0.2%)	0.100	10	1.0	8.7	9.0
	5Bs	0.0342	0.100	10	100.0	6.7	8.2
GB-6	6A	0.0342	0.00100	-	100.0	4.8	6.4
	6As*	0.0342	0.00159	10	100.0	5.0	6.5
	6Bs*	0.0342	0.00159	10	1.0	6.9	7.9
	6Cs	0.0342	0.00688	100	100.0	5.6	7.1
	6Ds	0.0342	0.00688	100	1.0	7.4	8.2
	6E	0.0342	(containing 10^{-5}m HCl)		N_2	5.1	5.2
	6F	0.0342	(containing 10^{-4}m HCl)		N_2	4.1	4.2
	6G	0.0342	(containing 10^{-3}m HCl)		N_2	3.1	3.2
	6H	0.0342	(containing 10^{-4}m NaOH)		N_2	9.9	7.2
	6I	0.0342	(containing 10^{-3}m NaOH)		N_2	10.9	8.2

*Solution used for aging tests

**From added sodium bicarbonate and carbonate and the injected Na_2S

Run NB-1

Solution A

TEMP	PCCO2	TC(PPM)	TS(PPM)	CNACL(M)	NAC(M)	GAM01	GAM02
25.	0.033	3186.	0.	0.	1.00E-01	1.000	1.000

TEMP	PH	CH2CO3	CHCO3	CCO3	CH2S	CHS	CS	COH	GAM1	GAM2
25.	9.86	1.1E-05	4.5E-02	2.8E-02				9.5E-05	0.760	0.410
285.	9.52	1.4E-03	6.9E-02	2.1E-03				2.7E-02	0.558	0.155

Solution B

TEMP	PCCO2	TC(PPM)	TS(PPM)	CNACL(M)	NAC(M)	GAM01	GAM02
25.	100.	5886.	0.	0.	1.00E-01	1.000	1.000

TEMP	PH	CH2CO3	CHCO3	CCO3	CH2S	CHS	CS	COH	GAM1	GAM2
25.	6.73	3.4E-02	1.0E-01	4.4E-05				7.0E-08	0.776	0.434
285.	8.25	3.5E-02	9.8E-02	1.6E-04				1.5E-03	0.546	0.147

Solution C

TEMP	PCCO2	TC(PPM)	TS(PPM)	CNACL(M)	NAC(M)	GAM01	GAM02
25.	100.	1533.	0.	0.	1.00E-03	1.000	1.000

TEMP	PH	CH2CO3	CHCO3	CCO3	CH2S	CHS	CS	COH	GAM1	GAM2
25.	4.83	3.4E-02	1.0E-03	3.5E-09				7.1E-10	0.965	0.871
285.	6.49	3.4E-02	9.8E-04	1.0E-08				1.5E-05	0.911	0.698

Run GB-1

Solution 1A

```
TEMP      PCCO2     TC(PPM)     TS(PPM)     CNACL(M)     NAC(M)     GAM01     GAM02

 25.       1.        4595.        0.         4.278      1.09E-01   2.440     3.820


TEMP  PH     CH2CO3  CHCO3    CCO3     CH2S     CHS      CS       COH      GAM1  GAM2

 25. 8.58  1.4E-04 1.0E-01 4.7E-03 1.6E-10 2.9E-08 3.7E-12 7.0E-06  0.549 0.202
285. 8.59  2.3E-03 1.0E-01 7.3E-04 5.6E-10 2.9E-08 2.4E-10 6.1E-03  0.287 0.039
```

Solution 1B

```
TEMP      PCCO2     TC(PPM)     TS(PPM)     CNACL(M)     NAC(M)     GAM01     GAM02

 25.      100.       5403.        0.         4.278      1.09E-01   2.440     3.820


TEMP  PH     CH2CO3  CHCO3    CCO3     CH2S     CHS      CS       COH      GAM1  GAM2

 25. 6.62  1.4E-02 1.1E-01 5.6E-05 1.0E-08 1.9E-08 2.7E-14 7.6E-08  0.549 0.203
285. 7.81  1.5E-02 1.1E-01 1.3E-04 3.1E-09 2.6E-08 3.6E-11 1.0E-03  0.287 0.039
```

Run GB-2

Solution 2A

```
TEMP      PCCO2      TC(PPM)      TS(PPM)      CNACL(M)     NAC(M)      GAM01      GAM02

 25.      100.         660.          0.          4.278      1.09E-03    2.440      3.820


TEMP  PH      CH2CO3   CHCO3    CCO3     CH2S     CHS      CS       COH       GAM1  GAM2

 25.  4.64  1.4E-02 1.1E-03 6.1E-09 2.9E-08 5.8E-10 8.4E-18 7.9E-10  0.550 0.203
285.  5.84  1.4E-02 1.1E-03 1.4E-08 2.7E-08 2.4E-09 3.6E-14 1.1E-05  0.288 0.039
```

Run GB-3

Solution 3A

TEMP	PCCO2	TC(PPM)	TS(PPM)	CNACL(M)	NAC(M)	GAM01	GAM02
25.		0.001 M HCL		4.278	0.		

TEMP	PH	CH2CO3	CHCO3	CCO3	CH2S	CHS	CS	COH	GAM1	GAM2
25.	3.26							3.3E-11	0.550	0.203
285.	3.54							5.4E-08	0.288	0.039

Solution 3B

TEMP	PCCO2	TC(PPM)	TS(PPM)	CNACL(M)	NAC(M)	GAM01	GAM02
25.	0.	0.	0.	4.278	0.001		

TEMP	PH	CH2CO3	CHCO3	CCO3	CH2S	CHS	CS	COH	GAM1	GAM2
25.	10.74							1.0E-03	0.550	0.203
285.	7.81							1.0E-03	0.288	0.039

Solution 3C (=1A)

TEMP	PCCO2	TC(PPM)	TS(PPM)	CNACL(M)	NAC(M)	GAM01	GAM02
25.	1.	4595.	0.	4.278	1.09E-01	2.440	3.820

TEMP	PH	CH2CO3	CHCO3	CCO3	CH2S	CHS	CS	COH	GAM1	GAM2
25.	8.58	1.4E-04	1.0E-01	4.7E-03	1.6E-10	2.9E-08	3.7E-12	7.0E-06	0.549	0.202
285.	8.59	2.3E-03	1.0E-01	7.3E-04	5.6E-10	2.9E-08	2.4E-10	6.1E-03	0.287	0.039

Run GB-3 (cont.)

Solution 3Cs

```
TEMP      PCCO2     TC(PPM)      TS(PPM)      CNACL(M)      NAC(M)      GAM01     GAM02

 25.        1.       4623.         10.          4.278      1.10E-01     2.440     3.820

TEMP    PH      CH2CO3   CHCO3    CCO3     CH2S      CHS      CS       COH       GAM1   GAM2

 25.  8.58   1.4E-04 1.0E-01 4.8E-03 1.6E-06 2.9E-04 3.7E-08 7.0E-06   0.549 0.202
285.  8.60   2.3E-03 1.0E-01 7.4E-04 5.5E-06 2.9E-04 2.4E-06 6.2E-03   0.287 0.039
```

Solution 3Ds

```
TEMP      PCCO2     TC(PPM)      TS(PPM)      CNACL(M)      NAC(M)      GAM01     GAM02

 25.      100.       5439.         10.          4.278      1.10E-01     2.440     3.820

TEMP    PH      CH2CO3   CHCO3    CCO3     CH2S      CHS      CS       COH       GAM1   GAM2

 25.  6.62   1.4E-02 1.1E-01 5.7E-05 9.9E-05 1.9E-04 2.7E-10 7.7E-08   0.549 0.203
285.  7.81   1.5E-02 1.1E-01 1.3E-04 3.1E-05 2.6E-04 3.6E-07 1.0E-03   0.287 0.039
```

Run GB-4

Solution 4A (=2A)

```
TEMP     PCCO2     TC(PPM)     TS(PPM)     CNACL(M)     NAC(M)      GAM01     GAM02

 25.     100.        660.         0.         4.278      1.09E-03    2.440     3.820


TEMP   PH      CH2CO3   CHCO3    CCO3     CH2S     CHS      CS       COH       GAM1  GAM2

 25.  4.64   1.4E-02 1.1E-03 6.1E-09 2.9E-08 5.8E-10 8.4E-18 7.9E-10  0.550 0.203
285.  5.84   1.4E-02 1.1E-03 1.4E-08 2.7E-08 2.4E-09 3.6E-14 1.1E-05  0.288 0.039
```

Solution 4As

```
TEMP     PCCO2     TC(PPM)     TS(PPM)     CNACL(M)     NAC(M)      GAM01     GAM02

 25.     100.        685.        10.         4.278      1.68E-03    2.440     3.820


TEMP   PH      CH2CO3   CHCO3    CCO3     CH2S     CHS      CS       COH       GAM1  GAM2

 25.  4.81   1.4E-02 1.7E-03 1.4E-08 2.9E-04 8.7E-06 1.9E-13 1.2E-09  0.550 0.203
285.  6.02   1.4E-02 1.6E-03 3.1E-08 2.6E-04 3.5E-05 7.8E-10 1.6E-05  0.288 0.039
```

Solution 4Bs

```
TEMP     PCCO2     TC(PPM)     TS(PPM)     CNACL(M)     NAC(M)      GAM01     GAM02

 25.       1.         71.        10.         4.278      1.68E-03    2.440     3.820


TEMP   PH      CH2CO3   CHCO3    CCO3     CH2S     CHS      CS       COH       GAM1  GAM2

 25.  6.75   1.4E-04 1.5E-03 1.0E-06 8.1E-05 2.1E-04 4.0E-10 1.0E-07  0.550 0.203
285.  7.33   4.7E-04 1.1E-03 4.4E-07 7.8E-05 2.2E-04 9.7E-08 3.3E-04  0.288 0.039
```

Run GB-5

Solution 5A

TEMP	PCCO2	TC(PPM)	TS(PPM)	CNACL(M)	NAC(M)	GAM01	GAM02
25.	1.	4274.	10.	0.034	1.01E-01	1.000	1.000

TEMP	PH	CH2CO3	CHCO3	CCO3	CH2S	CHS	CS	COH	GAM1	GAM2
25.	8.69	3.4E-04	9.3E-02	3.9E-03	4.3E-06	2.9E-04	3.3E-08	6.5E-06	0.754	0.401
285.	8.99	5.7E-03	9.1E-02	8.8E-04	1.5E-05	2.8E-04	3.1E-06	8.4E-03	0.518	0.129

Solution 5B

TEMP	PCCO2	TC(PPM)	TS(PPM)	CNACL(M)	NAC(M)	GAM01	GAM02
25.	100.	5925.	10.	0.034	1.01E-01	1.000	1.000

TEMP	PH	CH2CO3	CHCO3	CCO3	CH2S	CHS	CS	COH	GAM1	GAM2
25.	6.73	3.4E-02	1.0E-01	4.6E-05	1.7E-04	1.2E-04	1.5E-10	7.0E-08	0.756	0.404
285.	8.23	3.6E-02	9.9E-02	1.7E-04	6.9E-05	2.2E-04	4.5E-07	1.5E-03	0.516	0.128

Run GB-6

Solution 6A

```
TEMP    PCCO2    TC(PPM)    TS(PPM)    CNACL(M)    NAC(M)     GAM01    GAM02

 25.    100.     1533.       0.         0.034      1.00E-03   1.000    1.000


TEMP  PH     CH2CO3  CHCO3   CCO3    CH2S    CHS     CS      COH      GAM1  GAM2

 25. 4.78  3.4E-02 1.0E-03 4.3E-09 2.9E-08 2.2E-10 2.5E-18 7.1E-10  0.841 0.547
285. 6.35  3.4E-02 9.9E-04 1.5E-08 2.8E-08 9.6E-10 1.7E-14 1.5E-05  0.652 0.236
```

Solution 6As

```
TEMP    PCCO2    TC(PPM)    TS(PPM)    CNACL(M)    NAC(M)     GAM01    GAM02

 25.    100.     1558.      10.         0.034      1.59E-03   1.000    1.000


TEMP  PH     CH2CO3  CHCO3   CCO3    CH2S    CHS     CS      COH      GAM1  GAM2

 25. 4.97  3.4E-02 1.6E-03 1.1E-08 2.9E-04 3.4E-06 6.0E-14 1.1E-09  0.841 0.545
285. 6.54  3.4E-02 1.6E-03 3.8E-08 2.8E-04 1.5E-05 4.2E-10 2.4E-05  0.650 0.234
```

Solution 6Bs

```
TEMP    PCCO2    TC(PPM)    TS(PPM)    CNACL(M)    NAC(M)     GAM01    GAM02

 25.      1.       78.      10.         0.034      1.59E-03   1.000    1.000


TEMP  PH     CH2CO3  CHCO3   CCO3    CH2S    CHS     CS      COH      GAM1  GAM2

 25. 6.93  3.4E-04 1.4E-03 8.6E-07 1.4E-04 1.5E-04 2.4E-10 1.0E-07  0.841 0.545
285. 7.89  8.8E-04 8.9E-04 4.8E-07 1.4E-04 1.6E-04 9.9E-08 5.4E-04  0.651 0.235
```

Solution 6Cs

TEMP	PCCO2	TC (PPM)	TS (PPM)	CNACL (M)	NAC (M)	GAM01	GAM02
25.	100.	1785.	100.	0.034	6.88E-03	1.000	1.000

TEMP	PH	CH2CO3	CHCO3	CCO3	CH2S	CHS	CS	COH	GAM1	GAM2
25.	5.59	3.4E-02	6.7E-03	1.9E-07	2.8E-03	1.4E-04	1.0E-11	4.7E-09	0.833	0.530
285.	7.14	3.4E-02	6.3E-03	6.2E-07	2.4E-03	5.1E-04	5.9E-08	9.7E-05	0.636	0.220

Solution 6Ds

TEMP	PCCO2	TC (PPM)	TS (PPM)	CNACL (M)	NAC (M)	GAM01	GAM02
25.	1.	217.	100.	0.034	6.88E-03	1.000	1.000

TEMP	PH	CH2CO3	CHCO3	CCO3	CH2S	CHS	CS	COH	GAM1	GAM2
25.	7.43	3.4E-04	4.6E-03	8.8E-06	6.7E-04	2.3E-03	1.2E-08	3.2E-07	0.833	0.530
285.	8.25	1.5E-03	3.5E-03	4.4E-06	7.9E-04	2.2E-03	3.2E-06	1.2E-03	0.637	0.222

Solution 6E

TEMP	PCCO2	TC (PPM)	TS (PPM)	CNACL (M)	NAC (M)	GAM01	GAM02
25.		1.0E-05 M HCL		0.034			

TEMP	PH	CH2CO3	CHCO3	CCO3	CH2S	CHS	CS	COH	GAM1	GAM2
25.	5.07							1.4E-09	0.843	0.550
285.	5.18							1.0E-06	0.654	0.239

Run GB-6 (cont.)

Solution 6F

```
TEMP     PCCO2      TC(PPM)     TS(PPM)      CNACL(M)      NAC(M)      GAM01      GAM02

 25.            1.0E-04 M HCL               0.034


TEMP   PH      CH2CO3  CHCO3   CCO3    CH2S     CHS      CS       COH      GAM1   GAM2

 25.  4.07                                                      1.4E-10  0.843  0.550
285.  4.18                                                      1.1E-07  0.654  0.238
```

Solution 6G

```
TEMP     PCCO2      TC(PPM)     TS(PPM)      CNACL(M)      NAC(M)      GAM01      GAM02

 25.            1.0E-03 M HCL               0.034


TEMP   PH      CH2CO3  CHCO3   CCO3    CH2S     CHS      CS       COH      GAM1   GAM2

 25.  3.07                                                      1.4E-11  0.841  0.547
285.  3.19                                                      1.1E-08  0.652  0.236
```

Solution 6H

```
TEMP     PCCO2      TC(PPM)     TS(PPM)      CNACL(M)      NAC(M)      GAM01      GAM02

 25.                                        0.034       1.00E-04


TEMP   PH      CH2CO3  CHCO3   CCO3    CH2S     CHS      CS       COH      GAM1   GAM2

 25.  9.93                                                      1.0E-04  0.843  0.550
285.  7.16                                                      1.0E-04  0.654  0.236
```

Run GB-6 (cont.)

Solution 6I

```
TEMP    PCCO2    TC(PPM)    TS(PPM)    CNACL(M)    NAC(M)     GAM01    GAM02

 25.                                    0.034     1.00E-03


TEMP  PH     CH2CO3  CHCO3   CCO3    CH2S    CHS    CS      COH      GAM1  GAM2

 25.10.92                                                  1.0E-03  0.841 0.547
285. 8.16                                                  1.0E-03  0.652 0.236
```

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